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OLD WEST REGIONAL COMMISSION

**TRACE ELEMENT EFFECTS OF
ENERGY CONVERSION FACILITIES:**

Phase One Report

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TRACE ELEMENT EFFECTS OF
ENERGY CONVERSION FACILITIES:

A Phase One Final Report to the
Old West Regional Commission

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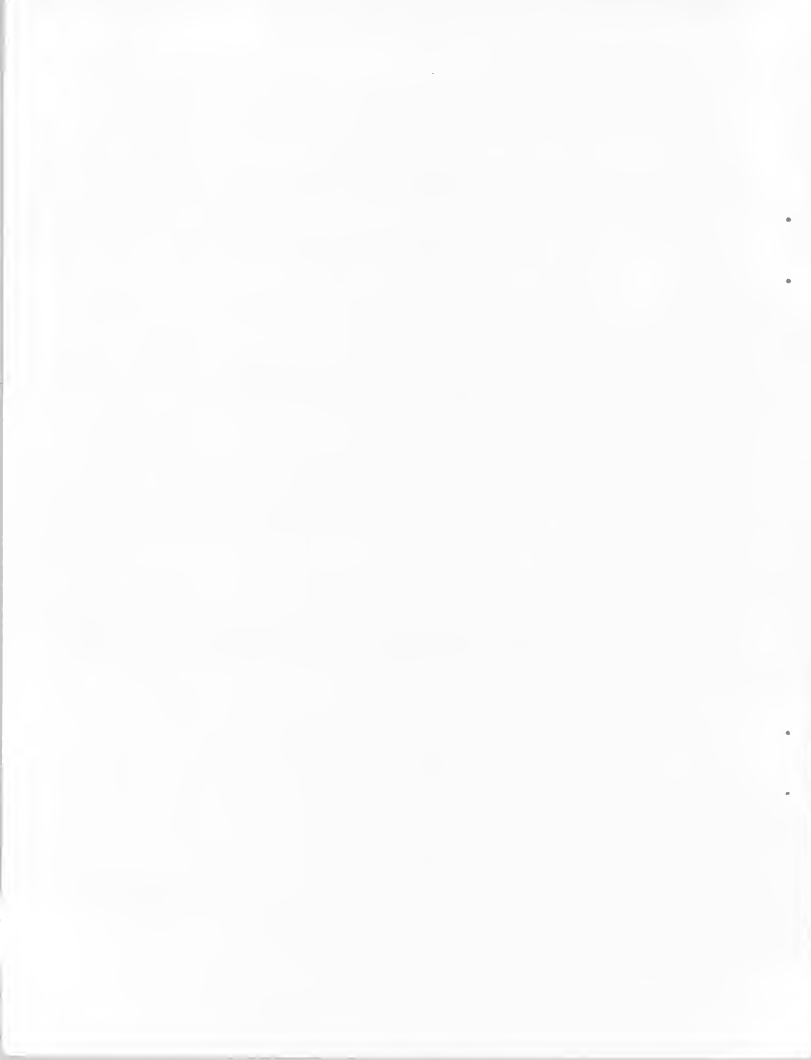
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ABSTRACT

This study was performed in a 2400 square mile area of western North Dakota to evaluate the potential significance of 15 trace elements (As, Be, Cd, Cr, Cu, F, Pb, Hg, Mo, Ni, Se, S, U, V, Zn) released to the environment through the energy conversion of coal. The methodology for evaluating these trace elements included the analysis of coal from four coal mines; the study of operating histories and design parameters of six lignite-fired electrical generating facilities; and the analysis of soil taken from 205 locations within the study area.

The concentration of trace elements in the coal and facility design parameters served as input data for a climatological dispersion model with a deposition function for estimating the dry deposition of trace elements to the study area. Trace element deposition was compared to existing soil concentrations. The application of a climatological dispersion-deposition model demonstrated that modern era energy conversion facilities contribute three orders of magnitude less surface deposition than do energy conversion facilities designed and operated since the 1920's.

This report presents a methodology for determining the significance of individual trace elements released to the environment through the energy conversion of coal. For short-

term (annual projections), the projected depositions on environmental receptors are not expected to cause adverse effects on ecosystems. However, equating the potential long-term environmental significance of the quantities of these trace elements deposited to the environment remains for further evaluation as part of this continuing research effort being conducted in cooperation with the Old West Regional Commission.

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INTRODUCTION

Background

The conversion of energy, from a stored or potential source in nature, to a useable form has been and will continue to be a challenge to man in meeting "supply-demand" requirements. The availability of energy is necessary to the sustaining of the nation's posture in the world. An abundant supply of energy represents, in the world economy, a major factor for future growth and development in an ever-increasing technological society. One need only to examine the increasing dependence that has been placed upon energy availability in recent years.

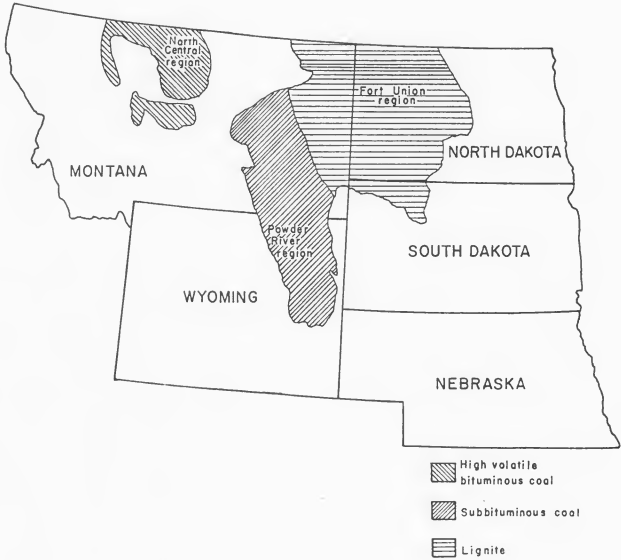
In the United States today, there are various predictions concerning reserves of oil and natural gas. While these predictions vary, there appears to be agreement that the supply of domestic oil and natural gas is limited and may not be able to meet increasing demands, or needs, for energy in the future. In addition, the dependence upon other countries "rich in energy" does not appear to be an acceptable alternative to maintaining an adequate supply of fossil fuels. Attention has been directed to the development and utilization of coal in the energy conversion process. Although other types of energy conversion processes, for example nuclear and solar, are being considered more aggressively; it appears that a fossil-fueled energy supply will continue to be the primary source of energy, with greater emphasis placed on the utilization of coal.

Development and utilization of coal reserves of this region is underway, with even more significant utilization projected. The "mine-mouth" production of coal for electrical generation and the conversion of coal to synthetic fuels pose environmental questions specifically for the states of Montana, Wyoming, and North Dakota. The significance of these environmental questions is emphasized by the expanse of coal reserves which are or could potentially be utilized within these states as shown in Figure 1. The environmental questions of coal utilization are not unique to these three Old West Region states since the states of South Dakota and Nebraska will, no doubt, be using some of the coal exported from the other three states richer in coal deposits. An example of this export-import relationship is the transportation of coal from southwestern North Dakota to a power generating station in northeastern South Dakota. It does appear that environmental questions will be regional in scope. Further, distribution of airborne contaminants is not restricted by geographical boundaries.

Much of the attention of the environmental impact of coal resource development has been concentrated on the more conventional, or historic effects of environmental contamination. The emphasis has been on the direct effects of contaminants such as particulates and sulfur dioxide. Little attention has been devoted to the effect of trace element translocation and enrichment in the environment of living organisms.

FIGURE 1

COAL PRODUCTION AREAS OF THE OLD WEST REGION



SOURCE: Federal Energy Administration 1975

Considerable chemical and physical analysis has been performed on the coals of this region, with emphasis on the assessment of the energy potential of coal. Analytical tests on coal have been largely confined to determination of the chemical composition, physical properties, and behavior of coals as they relate to the combustion process. These tests include the proximate analysis (volatile matter, fixed carbon, ash, sulfur, BTU/lb., and moisture content) and the ultimate analysis (chemical elements - including hydrogen, carbon, sulfur, oxygen, nitrogen, ash and moisture). Other typical analyses include: friability, grindability, screen sizing, free swelling and ash fusibility of the coal.

Coal contains other chemical elements in varying "trace" concentrations. It is toward these trace concentrations that this study is directed. Trace elements can generally be defined as those elements present in materials in concentrations of 1,000 parts per million (ppm) or less. Although these elements are called "trace elements" they may be as important to the energy development question as the energy potential of the coal itself. Any chemical element, when released into the environment becomes a part of the environment; and due to the chemical properties of the particular element considered, it tends to move within the environmental food chains of living organisms.

Trace elements are found throughout the environment. Soil, for example, is a mixture of "natural" trace elements which, in the agricultural setting, are utilized in the production of food and fiber. Increases in the concentration of the natural chemical elements in the soil, through contamination, has resulted in deleterious effects (Bauchauer, 1973; Churchill et al., 1948; Dunn et al., 1932; Hammond and Aronson, 1964). The deleterious effects are a function of the specific trace element concentrations, both natural and enriched; and the duration of the contaminating event.

As a result of recent interest in trace elements, these chemical elements have generated fears concerning future energy development. These fears exist even though some of these elements are essential for proper nutritional-biological functioning, i.e., essential for health and life. In the case of animal health, for example, this group of essential elements includes chromium, cobalt, copper, iodine, iron, manganese, molybdenum, selenium, and zinc (Frieden, 1972). Deficiencies of essential trace elements have occurred when the nutritional availability of trace elements has changed. Excessive concentrations of some elements have been demonstrated to interfere with the normal availability of the essential trace elements, thereby creating a deficiency condition. It is necessary, therefore, that the trace element effects of energy conversion facilities be examined for assessment of environmental impact.

Energy Development

Energy development activities are projected to increase markedly within the states of this region. The Northern Great Plains Resources Program, 1974, (NGPRP) considered the question of the magnitude of coal development in this region. Three levels of development were addressed by the NGPRP: Base, Most Probable, and Extensive. Excerpts from the Most Probable projections are presented in Tables 1, 2, and 3. Examination of these tables yields a numerical projection of future coal utilization. From Table 1, the Most Probable regional installed electrical generating capacity increase would be on the order of four to ten times existing (1974 base) capacities by the years 1985 and 2000, respectively. Increases in generating capacity means greater coal utilization, even when considering improvements in the thermal efficiency of future generating stations. Increase of coal utilization subsequently results in increased emission of process wastes, even when best available control technology is applied.

With respect to the production of synthetic natural gas from coal, the NGPRP has projected, from Table 2, that the most probable regional gasification capacity would be 1750 and 4000 million standard cubic feet of gas per day (MMSCFD) for the years 1985 and 2000, respectively. The nominal gasification plant size, under design consideration today, is 250 MMSCFD; this means that the number of plants projected for 1985 and 2000 are 7 and 16, respectively. In Table 3, these plant numbers are

TABLE 1
PROJECTED INSTALLED ELECTRICAL GENERATING CAPACITY

State	Installed Capacity in Megawatts		
	Existing January 1974	Most Probable 1985	Most Probable 2000
Montana	345	3101	9100
Nebraska	1534	3670	6920
North Dakota	862	4125	14910
South Dakota	252	1504	6060
Wyoming	1535	3893	8455
Regional Total	4528	16293	45445

SOURCE: Northern Great Plains Resources Program
Atmospheric Aspects Work Group Report
December 1974

TABLE 2
ESTIMATED GASIFICATION CAPACITY

State	Estimated Gasification Capacity (MMSCFD)		
	Existing January 1974	Most Probable 1985	Most Probable 2000
Montana	0	750	1500
North Dakota	0	500	1750
Wyoming	0	500	750
Regional Total	0	1750	4000

SOURCE: Northern Great Plains Resource Program
Atmospheric Aspects Work Group Report
December 1974

TABLE 3
GASIFICATION DEVELOPMENT FORECAST

State (Most Probable)	1985		2000	
	Number of Plants	Coal ^{1/} Requirement	Number of Plants	Coal Requirement
Montana	3	22.2	6	46.3
North Dakota	2	20.1	7	69.7
Wyoming	2	15.5	3	24.2

^{1/} Million tons per year.

SOURCE: Northern Great Plains Resources Program
Atmospheric Aspects Work Group Report
December 1974

translated into projected coal requirements. The apparent variability of the total coal requirements per plant, as indicated from Table 3, is due to the type and quality of coal available.

Currently, there is no commercial gasification operation in the United States. The coal gasification industry would not only be a new industry to the Old West Region, but it would be new to the United States as well. The production of other synthetic fuels from coal, such as synthetic petroleum via the liquefaction process, is in various stages of research and development; however, this process has not progressed as rapidly as the synthetic natural gas process. It is also possible, in the years ahead, to see the coals of this region being utilized as a feed stock in the chemical industry, in addition production of synthetic fuels.

Environmental Protection

Coal conversion in this region, whether it be electrical energy from coal-fired generating stations or synthetic fuels and chemicals from gasification facilities represents a significant increase in the amount of coal utilized. As pointed out earlier, the utilization of coal in these energy conversion processes will result in increased emission of process wastes, even when the best available control technology is applied. In addition to the question of increases in total waste emissions, other environmental factors must be considered. Other

environmental factors including the location and density of energy conversion facilities within the respective states. Questions, such as how much development, where to site such developments, and the type and degree of control over environmental emissions from developments; are questions which must be carefully considered and resolved. To facilitate the "proper" decision-making process, "best judgment" must be applied. Obviously, the fewer the unknowns, the better the judgment.

From the air pollution standpoint, traditional contaminants produced by coal utilization processes, such as particulates and sulfur dioxide, have been studied at considerable length. Control mechanisms, emission limitations, and ambient air quality standards exist for these contaminants in all states of this region. Control technology, when combined with proper facility siting, can be effective in preventing the adverse environmental aspects associated with these contaminants. Emission limitations and/or ambient standards are all but non-existent with respect to specific trace elements.

Although it is possible to have a direct trace element effect on living organisms from either an acute or chronic exposure to these contaminants (similar to that of the particulate or sulfur dioxide contaminants), trace elements can also cause an indirect effect via their translocation in the ecosystem food chain of living organisms.

It would appear that trace element decisions to this point in time, have been generally based upon case histories, isolated incidents, or unsupported assumptions that trace elements will be of little significance. Study of the trace element concentrations involved with coal development and the effect of these concentrations on living organisms must be addressed to eliminate fears, where fears are not warranted; and/or to evaluate more thoroughly the controls which will have to be applied to trace element emissions presenting potential problems. Some of the trace elements in coal will not be of significant concentration or specific chemical form to be of concern. The potential trace element effects will be a function of the concentration, chemical properties, and the mechanism of control of waste discharges to the environment.

There is a need, within this region, to evaluate emission control limitations and environmental quality standards for trace elements. Of the states in this region, only Montana and Wyoming have established numerical ambient air quality standards for air contaminants which could be classified as trace elements. These are: lead, beryllium, and hydrogen fluoride, in the case of Montana; and hydrogen fluoride in the case of Wyoming. In the North Dakota Ambient Air Quality Standards, the limiting of potential effects from trace elements is covered in general terms, with the following language:

"The ambient air shall not contain air contaminants in concentrations that would be injurious to human health or well-being or unreasonably interfere with the enjoyment of property or that would injure plant or animal life."

This statement does not specifically address trace elements in terms of chemical contaminants, nor is an assigned "standard" concentration established. Further, the implementation of a general standard such as this, is based upon "after-the-fact" problems, rather than a more desirable preventative standard.

Scope of this Study

The decision-making process involved in the review and evaluation of a proposed energy conversion facility is site specific. The decision concerning a proposed project, from the environmental standpoint must be based upon the type coal utilization process proposed, the specific characteristics of the coal used, the environmental controls exercised and final disposition of waste discharges. These site specific variables preclude the direct application of the results of this study to individual localized situations. Each "site specific" decision will have to be made on its own merits. This study proposes to remove unknowns from, and to provide a factual mechanism for, the decision-making process as it relates to potential effects of trace elements on living organisms. In this world of probabilities, there are few human decisions which are based upon absolutes. Removal of unknowns, however, will enhance the

decision-making process while reducing the risks associated with such decisions.

Considerable research information on trace elements is available in the literature as demonstrated in the Appendices of this report. Much of this information, although useful, cannot be directly utilized in the decision-making process. The information in the literature crosses many technical and scientific disciplines. There is no unifying of this information into one single systematic utilization of basic and applied research to the point of assessing the potential effects of environmental trace elements from coal development.

Resources limited resolution of all questions related to the effects of trace elements from energy conversion facilities. This study was designed to build upon the existing data and research base; to acquire additional detailed trace element data; to analyze the potential for environmental enrichment of the trace elements; and, to determine the potential trace element effects of coal development. The trace elements under consideration in this study include: arsenic, beryllium, cadmium, chromium, copper, fluoride, lead, mercury, molybdenum, nickel, selenium, sulfur, uranium, vanadium, and zinc.

Study Objectives

The objectives of this study focus on determining the effects of trace elements environmentally redistributed through the energy

conversion process. These objectives will enable the states of this region to plan for, regulate and otherwise prevent adverse environmental impacts on our citizens and the agricultural communities of the respective states. Regardless of the type coal-to-energy conversion process, trace elements pose a number of questions related to both short and long-term effects. To this end, the specific objectives of this study are:

1. to identify potential-problem trace elements in coal,
2. to determine the trace element profile of soils,
3. to determine the rate and concentration buildup of trace elements in the soil reservoir from existing coal-fired power plants,
4. to determine, via modeling of air emissions of trace elements, projected soil reservoir buildup of trace elements; and
5. to examine the need for development of specialized control procedures and/or regulatory control procedures for trace element wastes from energy conversion facilities.

METHODS

An environmental laboratory of approximately 2,400 square miles in western North Dakota was employed to evaluate trace element translocation from energy conversion facilities. Characterized by a gently rolling topography, typical of the northern Great Plains; this area is desirable since there are no industrial or large population sources other than those related to the energy conversion facilities involved in this study. Figure 2 shows the geographical relationship of the study area to the State of North Dakota. All of the aspects of an evaluation of trace element emissions from energy conversion facilities, as shown in Figure 3, exist in this area. The lignite coal-fired thermoelectric generating stations located in the area allow the study of effects in both a historical as well as potential sense.

The scope of this study focused on two localized areas, Area A and Area B, each twenty miles in diameter, as shown in Figure 4. Field work consisted of the collection of coal and soil samples in these areas. The surrounding area, Area C, was also sampled. However, study funds limited extensive soil analysis. The samples were analyzed for fifteen specific trace elements.

The study of airborne translocation involved the analysis of the operating history as well as the current environmentally-related operations of lignite coal-fired power plants located in the

FIGURE 2

GENERAL TRACE ELEMENT STUDY AREA

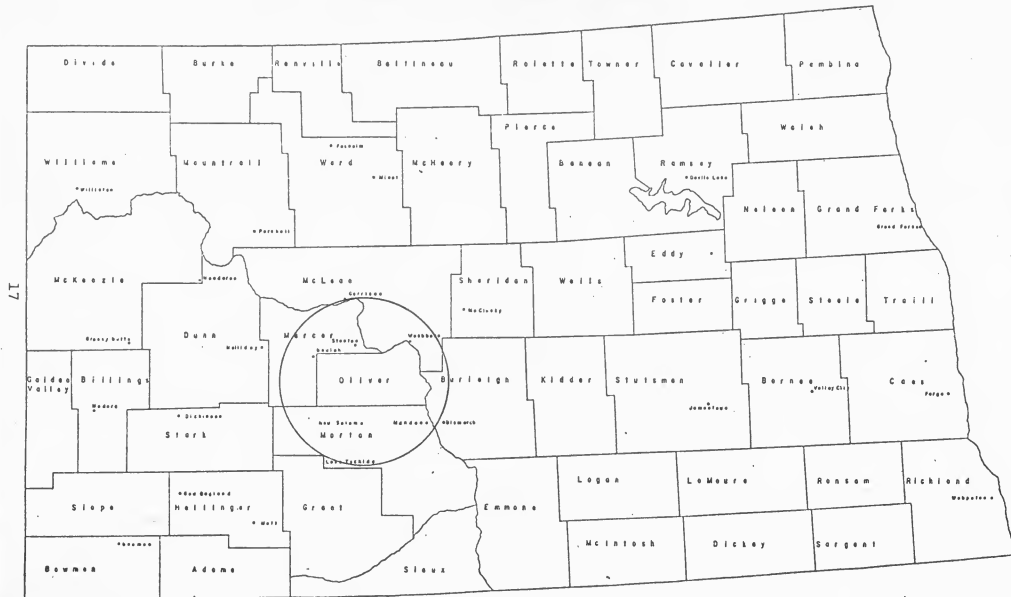


FIGURE 3
TRANSLOCATION OF TRACE ELEMENTS

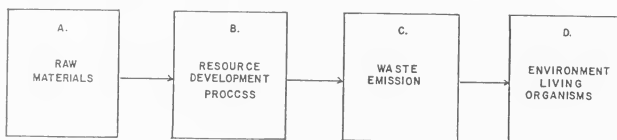
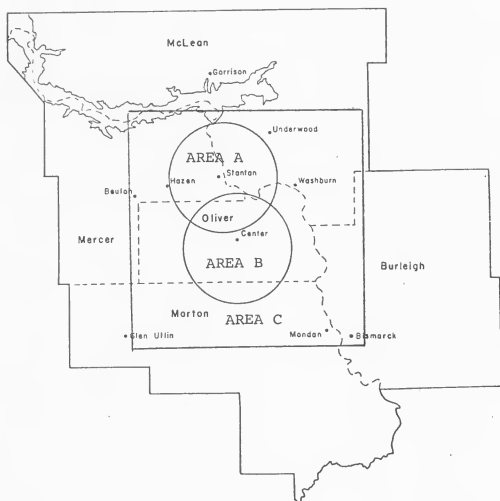


FIGURE 4
PROJECT STUDY AREA



study area. Analysis of the trace element emissions and subsequent deposition from these point sources was performed utilizing computer modeling and prediction techniques. An extensive review of the literature was also conducted to provide a basis for subsequent data analysis and interpretation.

Coal

The specific lignite producing mines selected for sampling are shown on Figure 5. These mines provide the fuel source for energy conversion facilities operating in the study area. At three of the mines, samples were collected from a recently exposed vertical seam face at three depth ranges as shown in Figure 6. The samples collected from the fourth mine were core samples taken by drilling vertically through the coal bed. The seam thickness of this mine averaged approximately thirteen feet with the cores being split to represent four depth ranges (0 to 3 feet, 3 to 6 feet, 6 to 9 feet, 9 to 13 feet). The sample collection at this mine is schematically illustrated in Figure 7.

All samples from Mines C-I, C-II, and C-III, were air dried, ground, and composited by equal weight to represent the various seam locations; e.g. surface, mid-seam, and base. In addition to the composite samples, a single sample representative of each depth range was retained and analyzed along with the composites for comparison of within seam trace element variations. All samples from Mine C-IV were individually air dried, ground, and

FIGURE 5
LIGNITE COAL MINE LOCATIONS



NOTE: CI through CIV indicate lignite mine locations

FIGURE 6

COAL SAMPLE COLLECTION, MINES C-I, C-II, C-III

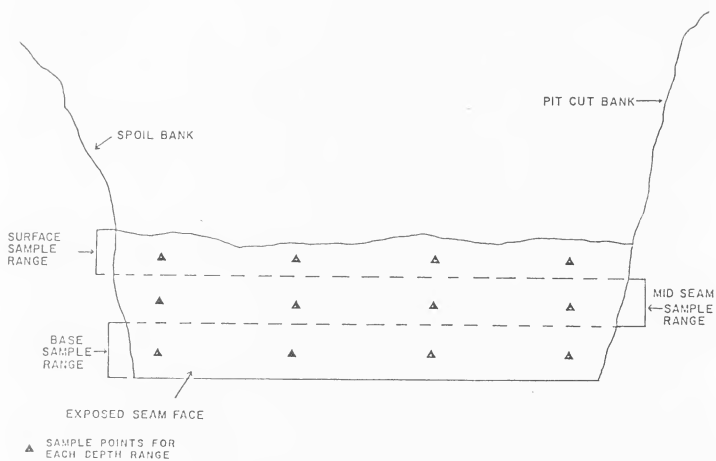
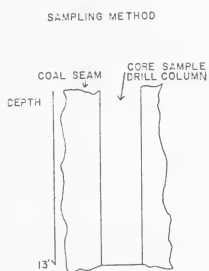
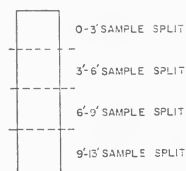


FIGURE 7
COAL SAMPLE COLLECTION, MINE C-IV



SAMPLE CORE SPLIT BY
SEAM DEPTH



submitted for analysis. In addition, a single composite sample was prepared by taking an equal weight of each individual sample and analyzed to show a general overview of the trace element concentrations from this mine.

The actual coal sample analysis was performed by a commercial laboratory. Of the fifteen study elements, arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), molybdenum (Mo), nickel (Ni), selenium (Se), vanadium (V), uranium (U), and zinc (Zn), were analyzed by spark source mass spectroscopy. Fluoride (F) analysis was performed by ion-specific electrode, sulfur (S) by the ESCHKA method for total sulfur and mercury (Hg) by atomic fluorescence.

The ESCHKA method of total sulfur analysis utilized in this project is that found in Part 26: ASTM Designation; D3177-75. In the procedure, a weighed coal sample and the ESCHKA reagent mixture are ignited together with the sulfur precipitated from the resulting solution as barium sulfate (BaSO_4). The precipitate is filtered, ashed, and weighed with the analytical results reported in weight percent total sulfur.

Total fluoride in coal was determined by oxygen bomb combustion. A coal sample was digested by combustion in an oxygen medium with the fluoride subsequently trapped in a small quantity of sodium carbonate solution. The bomb was washed and the fluoride

content of the washings determined by fluoride ion specific electrode measurements.

Mercury determination was performed through decomposition of the samples by combustion in an oxygen bomb. The mercury was subsequently absorbed in dilute nitric acid (3.75M) and analyzed by flameless atomic absorption. The remaining elements were analyzed by standard electrode molding techniques and spark source mass spectroscopy.

Energy Conversion Facilities

Within the environmental laboratory of the study area are six coal-fired electrical generating facilities. The locations of these facilities are shown in Figure 8. An extensive review of the physical design and operational history of each facility was performed in order to assess trace element soil enrichment from the emissions of these facilities. Of the six, three are located within the immediate study area, with the remaining facilities located on the perimeter. All six sources were operating or had operated prior to July 1, 1975.

Data collected for each facility consisted of physical design data and operational history, including annual hours of operation, periods of shutdown, sources of fuel, and annual coal usage since start up. Physical data included: stack heights, inside stack diameters, stack gas exit velocities, and stack gas

FIGURE 8

ENERGY CONVERSION FACILITIES LOCATED WITHIN STUDY AREA



exit temperatures, as well as types of emission control systems and their periods of operation since installation.

Information on the source of coal and annual fuel consumption was used in calculating trace element emission rates for each facility. The physical data and time periods of annual operations constitute climatological dispersion model inputs necessary for the mathematical projection of dispersion and resulting deposition patterns for the trace element emissions over the study area.

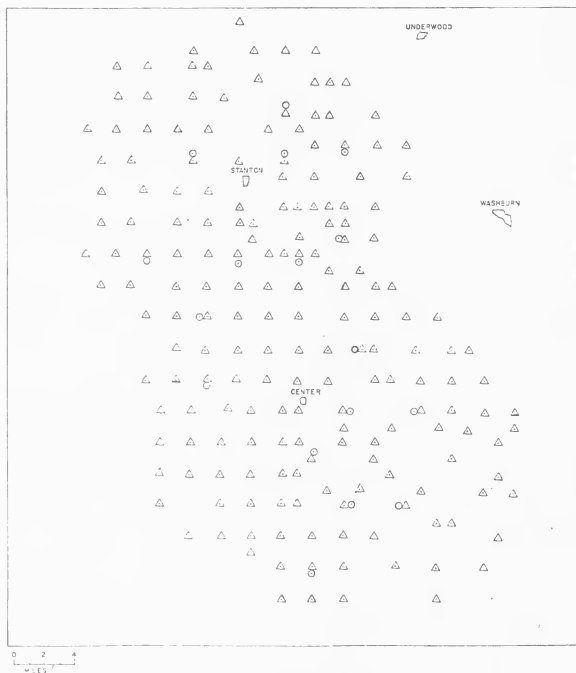
Soils

For the purpose of soil sampling, a grid system was established overlying the study area with collection points at approximately two mile intervals. Primarily, the soil samples were of native undisturbed soil. To assess the influence of agricultural activities on available soil concentrations of trace elements to crops and the possible influences of trace elements additions to the agricultural environment from energy conversion facilities, a number of soil samples from cultivated fields were collected throughout the study area.

A total of 205 locations were sampled throughout study areas A and B (See Figure 9a). Of these sites, 80% were sampled for single soil samples with 20% sampled for multiple soil samples. All single soil samples were collected at a depth of 0 to 3 inches. The multiple soil samples consisted of two 0 to 3 inch

FIGURE 9a

SOIL COLLECTION SITES



- Δ Undisturbed soil collection sites.
- Cultivated field soil collection sites.

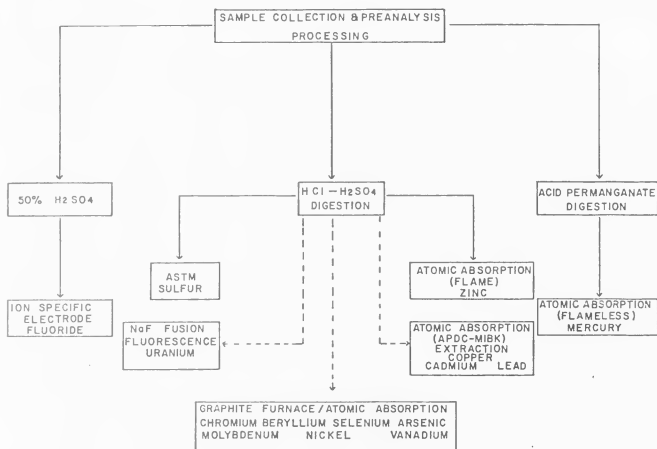
soil cores within a defined one square meter area and one soil core taken to a depth of 10 inches. The 10-inch soil core was split at the time of collection into three samples representing profile depths of 0 to 3 inches, 3 to 6 inches, and 6 to approximately 10 inches. At cultivated field soil collection sites, all samples were taken at multiple depths. The procedure involved taking a single core sample at a depth of 8 inches and splitting the core into two samples of 0 to 4 inch and 4 to 8 inch depth ranges.

At the time of sample collection, all materials were identified by site code number and brief descriptions of the sample entered in a field logbook. All samples were dried by spreading in stainless steel pans and exposed to the open air for varying lengths of time depending on the moisture content of the particular sample. After drying, the samples were weighed for total dry weight and ground to pass through a two millimeter sieve. The laboratory processing and analysis of all soil samples was performed in an identical manner.

The various analytical methodologies employed in the analysis of soil samples are presented in Figure 9b. The primary instrumentation consisted of Perkin-Elmer 403 and 503 atomic absorption spectrophotometers. Flameless atomic absorption procedures were performed with a Perkin-Elmer HGA 2100 graphite furnace in conjunction with both the 403 and 503 spectrophotometers.

FIGURE 9b

TRACE ELEMENT ANALYSIS OF SOILS



As shown in Figure 9b, soil samples were prepared for analysis by digestion with a 0.1 N acid mixture (0.05 N HCL + 0.25 N H₂SO₄), and a 1:10 ratio of soil to extractant. Zinc (Zn) was analyzed by flame atomic absorption using an acetylene flame while chromium (Cr), beryllium (Be), selenium (Se), arsenic (As), cadmium (Cd), lead (Pb), molybdenum (Mo), vanadium (V), and nickel (Ni), were analyzed using the HGA 2100 graphite furnace. Copper (Cu) was chleated and extracted with ammonium pyrrolidine dithiocarbamate-methyl isobutyl ketone (APDC-MIBK) and analyzed by atomic absorption using the acetylene flame.

Uranium (U) was analyzed by fluorescence involving a sodium fluoride fusion to a solid pellet. Sulfur (S) was analyzed by a commercial laboratory using a standard titrometric method. Mercury (Hg) analysis involved the treating of air-dried soil with a sulfuric acid-hydrogen peroxide-permanganate digestion (18N H₂SO₄-50% H₂O₂-5% KMnO₄). The mercury vapor generated was analyzed by the flameless atomic absorption methodology. A number of soil samples were shipped to a commercial laboratory for analysis of total fluoride. The procedure employed was steam distillation of the soil sample in a 50% sulfuric acid solution with subsequent analysis by ion specific electrode. Only twenty-five of the two hundred and five soil sample locations were analyzed for total fluoride.

Area-wide assessment of soil trace element enrichment from energy conversion facility emissions employed geochemical

mapping for eleven of the fifteen elements. Maps were not prepared for mercury (Hg), molybdenum (Mo), and selenium (Se), since greater than 30% of the total soil samples collected yielded analytical values less than the detectable limit of the methodology and instrumentation employed. With respect to fluoride, no geochemical mapping of soils was performed due to the small number of samples analyzed. The geochemical maps of the study area were drawn with a computer contour plotting software package. Using the soil sample collection grid system, each sampling interval was assigned a coordinate location relating to the X and Y axes of the sampling grid. The location coordinates and corresponding analytical data for each trace element comprised the computer data inputs.

Emissions Modeling

A computer dispersion model can be used to project and assess the trace element deposition within the study area from the nearby facility emissions (Vaughan, et al., 1975). The model serves as a tool to bridge the translocation of trace elements in the form of stack effluents from coal-fired facilities to ground level receptors. The particular model used in this study to compute ground level deposition is based upon techniques and methods developed by Turner, 1970, for the United States Environmental Protection Agency (EPA).

The discussion which follows identifies the procedure by which the Climatic Dispersion Model (CDM) was modified for the purpose

of projecting trace element deposition. A mathematical derivation is presented which allowed the use of an existing model capability (CDM) for the specific purpose of computing deposition.

The CDM computes the ground level concentration at a given ground level receptor from multiple point emission sources according to equation (1) below (Busse and Zimmerman, 1973).

$$(1) \quad \bar{C}_p = \frac{16}{\pi} \sum_{n=1}^n \sum_{l=1}^6 \sum_{m=1}^6 \frac{\phi(k_n, l, m) G_n S(\rho_n, z; U_1, P_m)}{\rho_n}$$

Where:

$$S(\rho_n, z; U_1, P_m) = \frac{2}{2\pi U_1 \sigma_z(\rho)} \left[\exp -\frac{1}{2} \left(\frac{h}{\sigma_z(\rho)} \right)^2 \right] \exp \left[\frac{-0.692 \rho_n}{U_1 T_{\frac{1}{2}}} \right]$$

- \bar{C}_p = ground level concentration due to n number of point sources ($\mu\text{g}/\text{m}^3$)
- $\phi(k_n, l, m)$ = joint frequency function for surface winds
- ρ_n = distance from receptor to nth point source (m)
- G_n = emission rate of nth point source (gm/sec)
- U_1 = wind speed (m/sec)
- h = effective stack height for nth point source (m)
- $\sigma_z(\rho)$ = vertical dispersion function (m)
- P_m = Pasquill stability category
- $T_{\frac{1}{2}}$ = half-life of pollutant (sec)

The decay or transformation of the pollutant is modeled in the expression by the depletion function:

$$(2) \quad \exp \left[\frac{-0.692 \rho_n}{U_1 T_{\frac{1}{2}}} \right]$$

This function can be used to represent the atmospheric residence times of particles emitted from stacks of specific coal-fired facilities.

Whelpdale, 1974, demonstrated a technique for computing particle residence times in the atmosphere through the formula:

$$(3) \quad C_t = C_o \exp [- (v_d/H) t]$$

C_t	=	concentration at ground level
C_o	=	initial concentration at time $t = 0$
v_d	=	deposition velocity (m/sec)
H	=	depth of mixing (m)

Whelpdale also points out that the quantity H/v_d is the atmospheric particulate residence time. The depth of mixing (H) of the pollutant particles is defined as the depth of the mixing layer, which varies with each of the six stability classes. Substituting the relationship of $U_1 = \rho_n/t$ into Equation (2), equating the resulting function to the exponential function is Equation (3), and solving for $T_{\frac{1}{2}}$ yields:

$$(4) \quad T_{\frac{1}{2}} = 0.692 (H/v_d)$$

The terminal fall speed (v_d) for particles (less than 29 μm diameter) falling under Stokes flow at standard conditions is taken from Perkins, 1974, as:

$$(5) \quad v_d = 0.003\rho D^2$$

v_d	=	terminal fall speed (cm/sec)
ρ	=	particle density (gm/cm^3)
D	=	particle diameter (μm)

For purposes of this study, the terminal fall speed is used interchangeably as the deposition velocity. Larger particles, or particles having higher density, will tend to fall out quicker resulting in greater surface deposition. However, the deposition velocity conceptually includes, not only fallout, but

scrubbing action of surface roughness (e.g.; trees, buildings, grass).

Under conditions of known effluent mass particle size for a specific coal-fired facilities, and depth of mixing layer, the half-life ($T_{1/2}$) can be determined. Thus the depletion function (2) represents the rate of atmospheric fallout of effluents emitted from a stack.

The dry deposition on ground level receptors (DD) is taken from Vaughan, et al., 1975, as:

$$(6) \quad DD = C_p v_d \Delta t$$

DD =	deposition ($\mu\text{g}/\text{m}^2/\text{sec}$)
C_p =	ground level concentration at a receptor from a single point source ($\mu\text{g}/\text{m}^3$)
v_d =	deposition velocity (m/sec)
Δt =	time over which deposition is to be calculated

The dry deposition conceptually represents atmospheric fallout and scrubbing action of surface receptors. Wet deposition has been modeled by other investigators to include scavenging of precipitation producing weather phenomena. Wet deposition has not been included in the modeling analysis of total deposition at this stage of this study.

The CDM computer analysis is site specific in that the stack height, stack diameter, stack exit gas velocity, stack gas temperatures, and effluent emission rate are input parameters.

The effluent emission rate (G_n) was calculated by the following formula:

$$(7) \quad G_n = (CC/N)/K \times (1-WL) \times TEC \times AC$$

G_n =	trace element emission rate ($\mu\text{g}/\text{sec}$)
CC =	coal consumption by the facility over N number of years of operation up through 1975 (tons)
K =	a constant; to convert units from years to seconds, and tons to grams
WL =	water loading in the feed coal (%)
TEC =	trace element concentration in feed coal ($\mu\text{g}/\text{g}$ of coal)
AC =	effluent ash trace element concentration (% of the feed coal concentration)

Since WL was not known for the coals used to feed the facilities in this study, it was assumed to be 35% in correspondence to Aresco et al., 1960. AC was assumed to be 80% of the mass of trace elements in feed coals which escaped emission control systems and exited the facility stack. This factor was applied in the calculation of deposition and may be unrealistically high for a few trace elements while low for others. (Andren et al., 1975; Fulkerson et al., 1975).

PRESENTATION OF DATA

Coal

The analytical values for all coal samples and element distributions are presented in Figures 10a through 10d. A summary of this data is presented on Table 4. A literature summary showing the ranges of element concentrations in lignite coal from North Dakota and various coal types from surrounding states is presented in Appendix A.

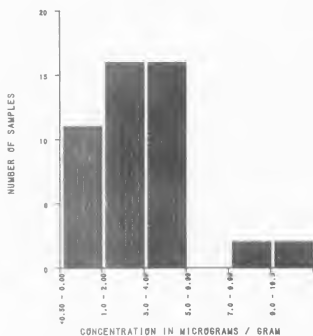
The results of other investigations presented on the literature composite (Table 4) cover a time span from 1935 to 1976. The wide variations in reported concentrations for many of the elements may be the result of marked advances in analytical technology in recent years. The results from this investigation show reasonable agreement with those of the Radian Corporation 1975, Basin Electric Power Cooperative 1972, and Ebasco Services, Incorporated 1973. This agreement arises from the use of comparable analytical methodologies to those employed in this study.

Energy Conversion Facilities

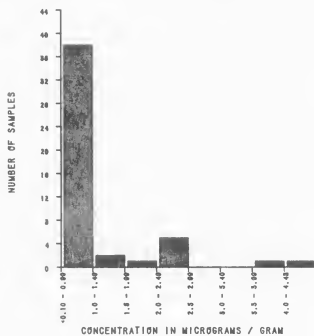
Energy conversion facilities constitute the primary industrial process whereby trace elements are introduced to the environment of the study area. In order to assess the possible soil enrichment of trace elements from the emissions of these facilities, it was necessary to develop an extensive review of

FIGURE 10a
FREQUENCY DISTRIBUTIONS OF TRACE ELEMENT CONCENTRATIONS
LIGNITE COAL

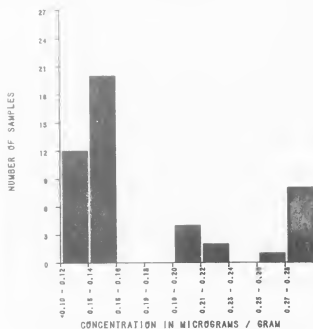
ARSENIC



BERYLLIUM



CADMIUM



CHROMIUM

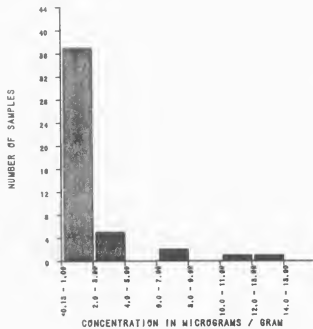
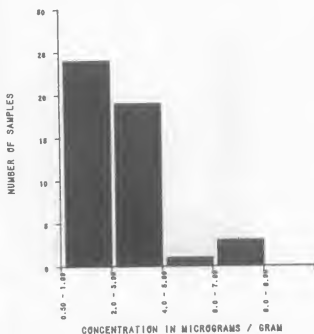
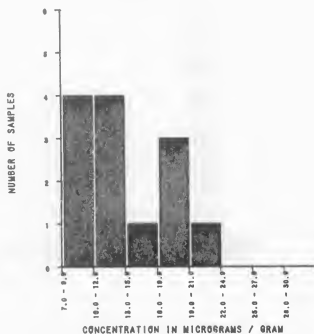


FIGURE 10b
FREQUENCY DISTRIBUTIONS OF TRACE ELEMENT CONCENTRATIONS
LIGNITE COAL

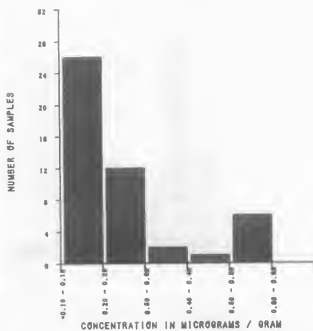
COPPER



FLUORIDE - TOTAL



LEAD



MERCURY

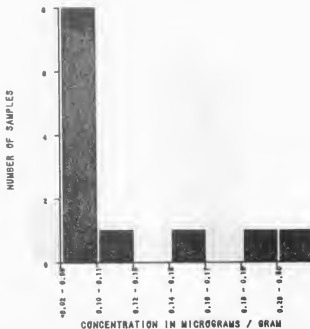
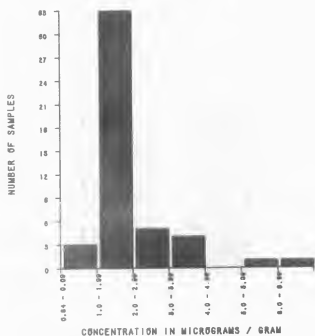
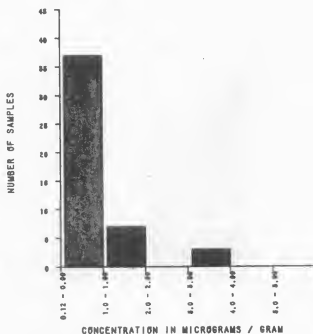


FIGURE 10c
FREQUENCY DISTRIBUTIONS OF TRACE ELEMENT CONCENTRATIONS
LIGNITE COAL

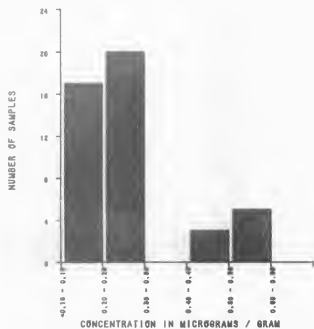
MOLYBDENUM



NICKEL



SELENIUM



URANIUM

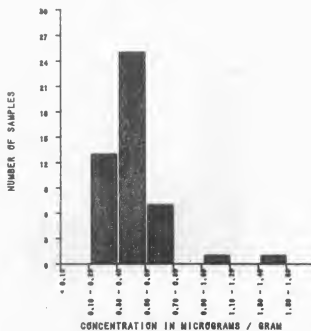


FIGURE 10d
FREQUENCY DISTRIBUTIONS OF TRACE ELEMENT CONCENTRATIONS
LIGNITE COAL

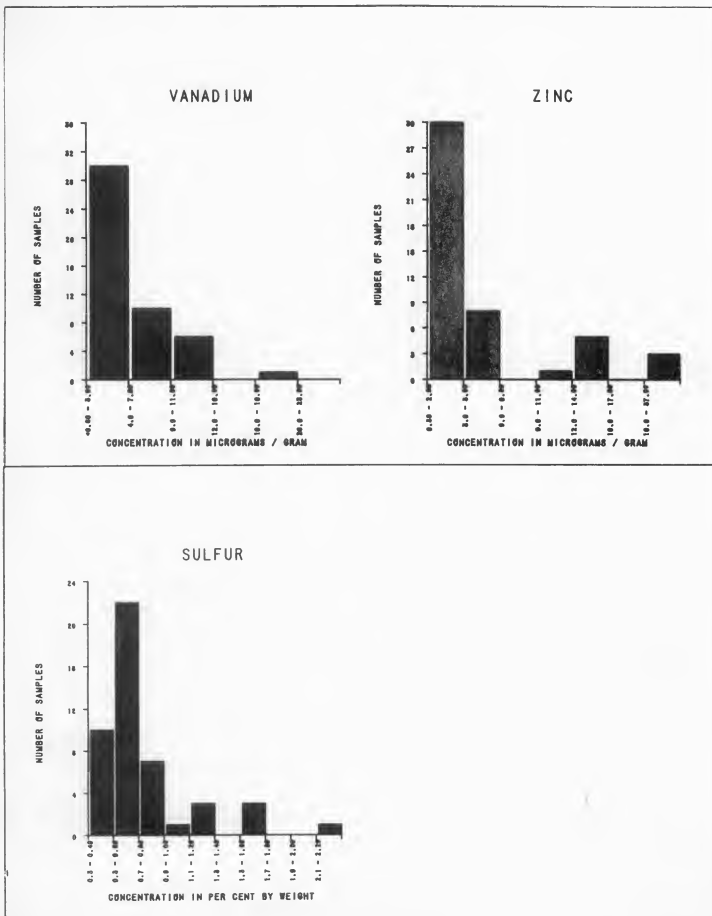


TABLE 4
COAL DATA SUMMARY

Element	Study Data ($\mu\text{g/gm}$)			Literature Summary ^{4/} ($\mu\text{g/gm}$)	
	Min.	Max.	Arithmetic Mean	Expected Average Conc. Range	
Arsenic	< 0.54	18.0	2.07	5.0	
Beryllium	< 0.10	4.3	0.75	0.1	- 4.0
Cadmium	< 0.10	0.27	0.13	0.10	- 0.53
Chromium	< 0.10	13.0	1.29	4.0	
Copper	0.53	7.7	2.88	< 1.0	- 40.
Fluoride ^{1/}	7.4	25.0	15.53	25.	- 150.
Lead	< 0.10	0.51	0.26	0.5	- 7.0
Mercury	< 0.02	0.28	<u>3/</u>	< 0.2	
Molybdenum	0.64	6.4	1.63	< 1.0	- 17.0
Nickel	0.12	5.8	0.93	1.3	- 40
Selenium	< 0.18	0.58	0.30	0.4	- 8.0
Uranium	< 0.10	1.4	0.47		
Vanadium	< 0.60	19.0	2.69	0.2	- 25.0
Zinc	0.30	37.0	2.56	2.9	
Sulfur ^{2/}	0.37%	2.29%	0.72%	< 0.7%	- 1.5%

^{1/} As total fluoride.

^{2/} As total sulfur, % weight.

^{3/} >30% of samples less than detectable limit, resulting in arithmetic mean which would fall below <0.02.

^{4/} Composite from literature search with averages from existing lignite coal data.

the physical design and operational history of each unit influencing the research area. A summary of this data for the six electrical generating stations influencing the study area is presented in Table 5.

The following information is a brief summary of each electrical generating facility considered in this investigation, along with schematics representing typical power plant designs. The schematics presented are not necessarily exact representations of the specific facilities in operation within the study area but are "typical" of that specific power plant design.

Facility P-I, began operation in the study area in late 1970. This is a 250 megawatt electrical generating unit located within the immediate study area and fired with lignite coal. The boiler arrangement is of the cyclone-fired type. A multi-cyclone system was used for fly ash control until mid 1975. A schematic of this type facility, including all inlet and outlet streams, is shown in Figures 11a and 11b with the exception of the 300 foot stack, Figures 11a and 11b are also applicable to Facility P-II. In mid 1975, the cyclone collection system of Facility P-I was removed and an electrostatic precipitator installed for control of particulate emissions. However, for the purpose of the trace element environmental deposition analysis, the emission control for this facility was multi-cyclone.

TABLE 5
SUMMARY OF ENERGY CONVERSION FACILITY
HISTORY AND STRUCTURAL DATA AS OF JULY 1, 1975

Facility	MW Capacity	Years of Operation	Total Raw Coal ^{1/} usage 7-1-75 tons	Average ^{1/} annual hours operation	Emission ^{2/} control devices	Mass particle size (dia in μ m)	Number of stacks	Height (ft)	Inside diameter (ft)	Gas exit temp ($^{\circ}$ F)	Gas exit velocity (ft/sec)
P-I	250	5	7,538,492	7,919	Multi-cyclone	10	1	300	19	330	70
P-II	85	21 12	3,525,000 3,900,000	8,000 8,000	Multi-cyclone	10	1 1	125 125	7 12	345 310	50 50
P-III	15	48 37 25	1,890,000 590,000 725,000	5,396 5,162 8,000	None None Mech. Dust Collector	20 ^{4/} 20 ^{2/} 10	2 1 2	74 87 74	5'6" 7'5" 5'6"	500 500 500	40 40 40
P-IV	180	9	7,018,037	7,426	Multi-cyclone	5	1	255	15	338	90
P-V	220	10	12,604,900	7,727	Multi-cyclone	5	1	350	15	350	74
P-VI ^{3/}	10	40	2,490,180	7,000	None	20 ^{4/}	1	80	6	350	50 ^{1/}

^{1/} Calculated and/or estimated from company information (annual coal usage times years of operation)

^{2/} Status as of July 1, 1975

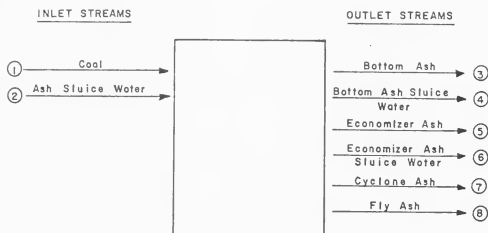
^{3/} Facility closed in 1969

^{4/} Available data indicate that 95% of stack particles have sizes less than 20 μ g.

SOURCE: Division of Environmental Engineering, North Dakota State Department of Health 1977

FIGURE 11a

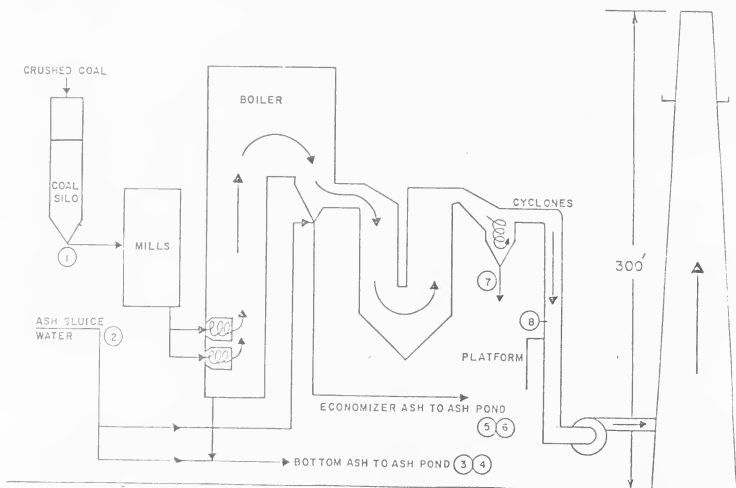
INLET AND OUTLET STREAMS OF ELECTRICAL GENERATING FACILITIES
SIMILAR IN DESIGN TO FACILITY P-I AND FACILITY P-II



SOURCE: Radian Corporation 1975

FIGURE 11b

DESIGN SCHEMATIC OF AN ELECTRICAL GENERATING FACILITY
SIMILAR IN DESIGN TO FACILITY P-I AND FACILITY P-II



SOURCE: Radian Corporation 1975, with modifications by the North Dakota State Department of Health.

Facility P-II began operations in 1954. This facility operated as a single unit with one 125 foot stack until 1963, when a second unit and an additional 125 foot stack were added. Both units operated with multi-cyclone collection systems for particulate emission control until late 1975. During 1975, the stacks on both units were replaced by 300 foot stacks, and one electrostatic precipitator installed on each boiler. However, for the purpose of the potential environmental deposition analysis, this facility was considered as multi-cyclone systems with 125 foot stacks.

Facility P-III has been in operation for a period of 48 years. P-III is the oldest of the five operating facilities in this study. Operations at this facility began in 1927 with the basic design as a two-unit facility with two 74 foot stacks and no emission control devices. In 1938, the facility was expanded with the addition of a third unit and an 87 foot stack. The facility maintained operation with three units until 1949 when two additional generating units and two additional 74 foot stacks were added. The additional units were equipped with mechanical dust collectors at installation. This comprises the operational status of Facility P-III as considered in this study.

In 1976, the stacks serving Units 3, 4, and 5, were replaced by a single 100 foot stack with an electrostatic precipitator replacing the mechanical dust collection system. A

schematic of the inlet and outlet streams for a typical electrical generating facility of the original design such as Facility P-III is presented in Figures 12a and 12b. These schematics are also applicable to the original design of Facility P-VI.

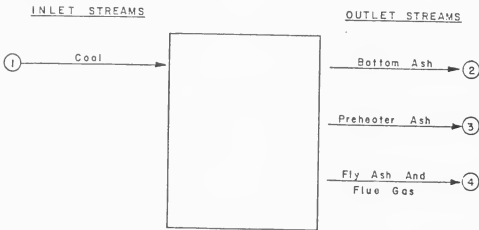
Facility P-IV has been in operation since 1966. This facility is located within the immediate study area and has operated as per the data presented on Table 5 through the initiation of this study in 1975. In 1976, the mechanical precipitator was replaced by an electrostatic precipitator for control of particulate emissions. Figures 13a and 13b present schematics of the inlet and outlet stream flows of an electrical generating unit similar to Facility P-IV. These schematics are also representative of the basic design of Facility P-V.

Facility P-V began its operation in early 1966. The initial emission control equipment consisted of a multi-cyclone system for particulate collection. In 1974 the system was replaced by an electrostatic precipitator. This facility was considered to operate from 1966 to 1975 as per the data presented in Table 5.

Facility P-VI was a small generating station which ceased operations in 1969. This facility was evaluated for its influence on the study area over an operational period from 1926 to 1969. This facility operated with two boiler units from 1926 to 1929 when a third unit was added. In 1945 a fourth boiler

FIGURE 12a

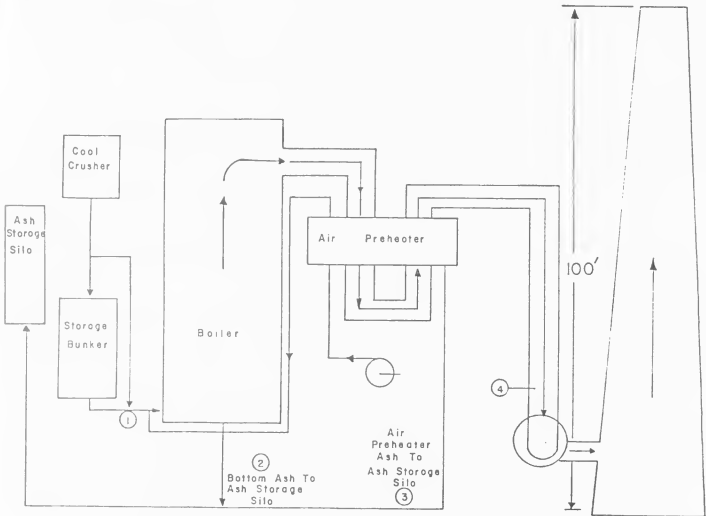
INLET AND OUTLET STREAMS OF ELECTRICAL GENERATING FACILITIES
SIMILAR IN DESIGN TO FACILITY P-III AND FACILITY P-VI



SOURCE: North Dakota State Department of Health, 1977

FIGURE 12b

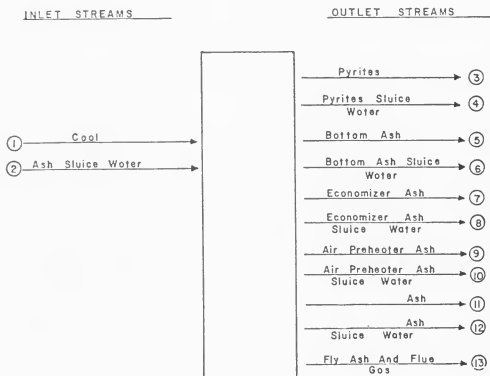
DESIGN SCHEMATIC OF AN ELECTRICAL GENERATING FACILITY
SIMILAR IN DESIGN TO FACILITY P-III AND FACILITY P-VI



SOURCE: North Dakota State Department of Health, 1977

FIGURE 13a

INLET AND OUTLET STREAMS OF ELECTRICAL GENERATING FACILITIES
SIMILAR IN DESIGN TO FACILITY P-IV AND FACILITY V



SOURCE: Radian Corporation 1975, with modifications by the
North Dakota State Department of Health.

DESIGN SCHEMATIC OF AN ELECTRICAL GENERATING FACILITY
SIMILAR IN DESIGN TO FACILITY P-IV AND FACILITY P-V



unit was added and the operation continued at this level until 1964 when the facility was temporarily closed.

Operations at Facility P-VI were resumed for a short period of time in 1967 with final closure coming in late 1969. Throughout the lifetime of this facility, it had an 80 foot stack and had been operated with no emission control devices. Records concerning coal usage and annual hours of operation are incomplete. These data presented in Table 5 for this facility consequently is an estimate with respect to these parameters as well as the stack gas exit velocity.^{1/}

During the time interval of this investigation, there were several 440 megawatt lignite-fired electrical generating facilities under construction. Since these facilities were not operational prior to this investigation, they were not considered in the environmental assessment of the potential trace element deposition.

Soil

The soil analytical results and sample range distributions are presented in Figures 14a through 14d. A summary of this data showing minimum, maximum and arithmetic mean concentrations in micrograms per gram as well as a literature composite of expected concentration ranges in "normal" soils is presented in Table 6. Appendix B is a presentation of a literature search providing the base data for establishment of ranges of concentrations for each trace element presented in Table 6.

^{1/} Personal Communication. 53

FIGURE 14a
FREQUENCY DISTRIBUTION OF TRACE ELEMENT CONCENTRATIONS
SURFACE SOILS

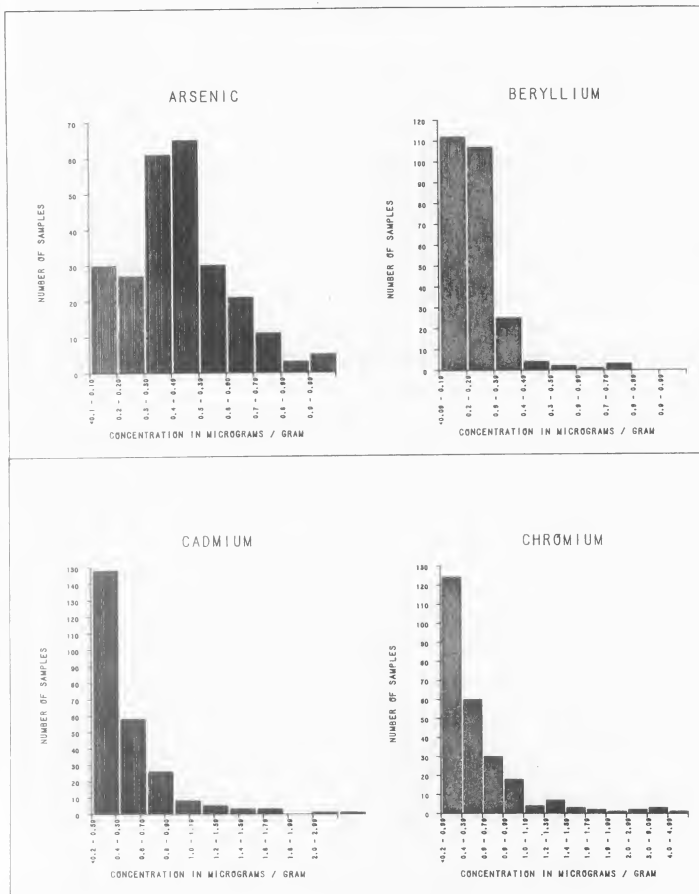


FIGURE 14b
FREQUENCY DISTRIBUTION OF TRACE ELEMENT CONCENTRATIONS
SURFACE SOILS

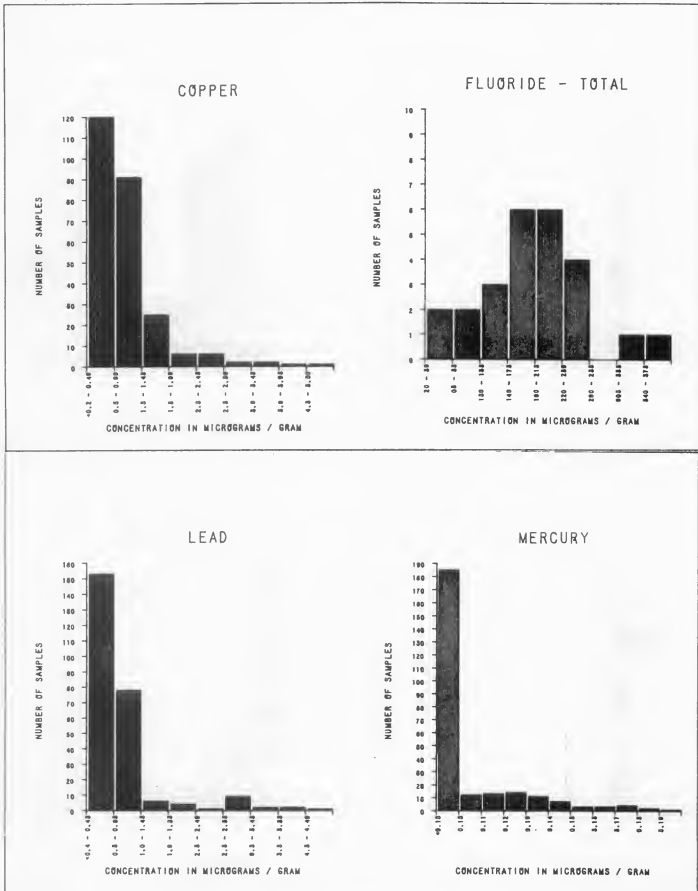
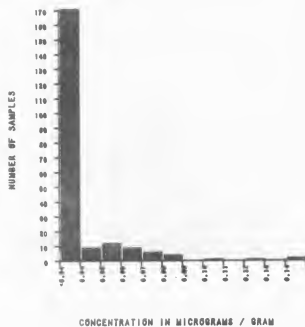
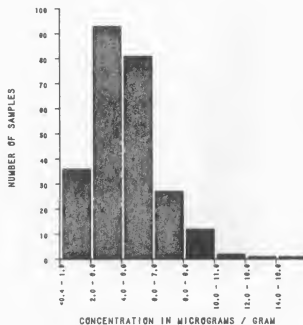


FIGURE 14c
FREQUENCY DISTRIBUTION OF TRACE ELEMENT CONCENTRATIONS
SURFACE SOILS

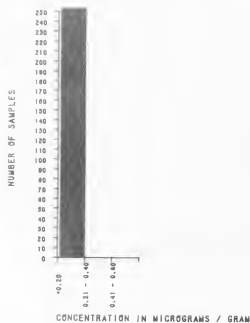
MOLYBDENUM



NICKEL



SELENIUM



URANIUM

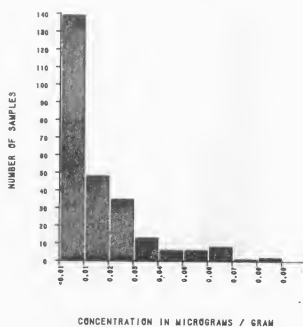


FIGURE 14d
FREQUENCY DISTRIBUTION OF TRACE ELEMENT CONCENTRATIONS
SURFACE SOILS

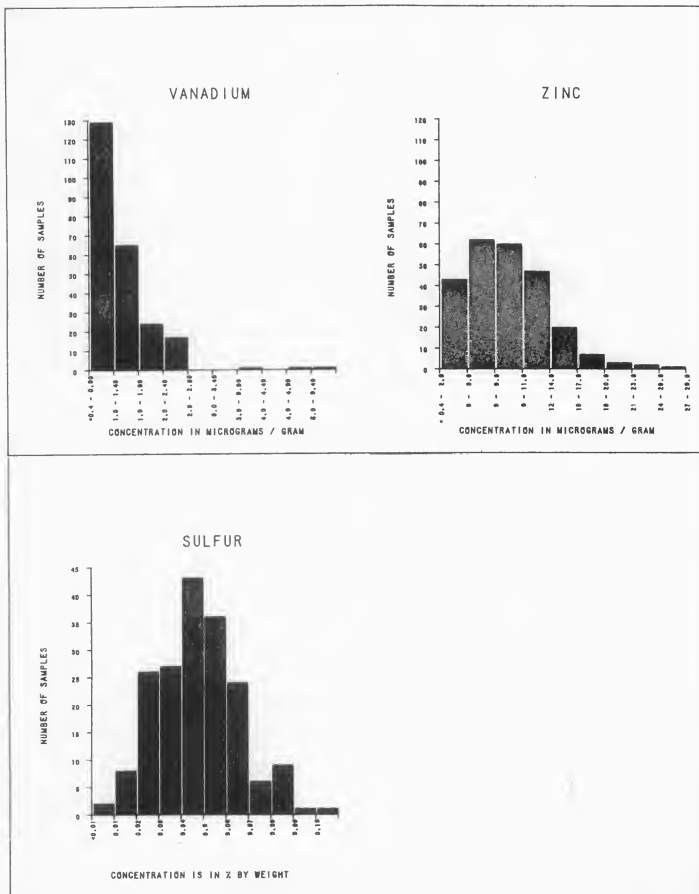


TABLE 6
SOIL DATA SUMMARY
SURFACE SAMPLES FROM 1975

	Study Data (µg/gm)			Literature Summary (µg/gm)		
	Min.	Max.	Arithmetic Mean	Expected	Average	Conc. ^{3/}
Arsenic	< 0.10	0.95	0.42	2.5	-	108.
Beryllium	< 0.08	0.76	0.21	0.1	-	40.
Cadmium	< 0.20	4.0	0.44	0.01	-	7.0
Chromium	< 0.20	4.90	0.52	1.0	-	100.
Copper	< 0.20	5.60	0.70	2.5	-	200.
Fluoride ^{1/}	23.0	360.0	172.44	100	-	300
Lead	< 0.40	4.48	4/	<0.5	-	15.0
Mercury	< 0.10	0.19	4/	<0.05	-	0.14
Molybdenum	< 0.04	0.14	4/	<0.10	-	5.0
Nickel	< 0.40	15.2	4.27	<1.0	-	100.
Selenium		<0.20	4/	0.10	-	6.0
Uranium	< 0.01	0.08	4/			
Vanadium	< 0.40	5.0	1.03	3.0	-	250.
Zinc	< 0.40	60.0	7.22	10.0	-	300.
Sulfur ^{2/}	< 0.01%	0.10%	0.04%	0.01%	-	0.06%

1/ Data presented as total fluoride.

2/ Data presented as total sulfur, % weight.

3/ Composite average from literature review.

4/ Greater than 30% of samples less than detectable limit giving a mean of less than (<) 0.01 limit for Uranium, <0.20 for Selenium, <0.04 for Molybdenum, <0.10 for Mercury, and <0.4 for Lead.

DISCUSSION

Coal

The Federal Energy Administration, 1975, has extensively described the Fort Union Coal Formation in the northern Great Plains. According to the FEA, the Fort Union region is the largest of the northern Great Plains coal producing areas. It encompasses the western half of North Dakota and parts of South Dakota and Montana. It has been estimated that the total lignite coal reserves in this region are approximately 440 billion tons, which makes it the largest coal reserve in the entire United States.

Most of the coal in North Dakota is found in the Lebo, Tongue River, and Sentinel Butte members of the Fort Union formation of Paleocene Age. A few thin lignite beds have also been found to occur near the base of the underlying Wasatch formation of Paleocene and Eocene Age, in the Basal Tullock member of the Fort Union formation, and the underlying Hellcreek formation of late Cretaceous Age.

The coal beds of western North Dakota are discontinuous and vary greatly in thickness. More than one hundred beds have been identified by the North Dakota Geological Survey, (1973), but only a small percentage of these are of commercial thickness. The Fort Union formation ranges in thickness from 425 to 775 feet in South Dakota up to 1,500 feet in some areas of eastern

Montana. The coal throughout most of the Fort Union region is lignite in rank. However, westward along the formation from the Montana-North Dakota boundary (see Figure 1), the rank of the coal increases to Sub-bituminous C near Miles City and Sub-bituminous B further west. The Fort Union region merges with the Powder River Basin along a vague northwest-trending boundary in east central Montana. This boundary is defined roughly by the change in rank of coal from lignite to sub-bituminous.

The trace element concentrations obtained through this study from specific mine sources of the Fort Union formation in western North Dakota have been shown to agree with the work of other investigators (as presented in Appendix A). The variation in analytical data that exists between the reported values in this investigation and those of the literature can be attributed to several factors. These factors include; the number of samples analyzed, treatment of the samples prior to analysis, the specific analytical instrumentation and methodology, the methods of statistical reduction of data, and most importantly the natural geochemical variation within and between the different coal beds investigated.

The geochemical variation found between coal beds and within the various seams of a specific bed is difficult to assess and largely depends upon the hydrology in the area of a given coal-producing seam. According to Nicholls, 1968, trace element accumulation in various coal seams and locations within coal

beds is based on groundwater circulation through seam margins, against surrounding strata, or against shale or dirt partings running through the various seams. Higher concentrations of trace elements usually occur in the outer edges of seams due to initial contact with circulating groundwater.

The geochemical variations of elements within a coal seam was not extensively studied in this investigation. However, this natural variation can be seen on Tables 7, 8, and 9, for Mines C-I, C-II, and C-III, respectively. These tables show the results of a composite sample and corresponding single sample for each of the depth ranges at Mines C-I, C-II, and C-III. This geochemical variation becomes significant when trace element emission calculations for energy conversion facilities are based on trace element concentrations in feed coal. The data in these tables demonstrate that the calculation of emissions could show an extremely wide range in expected rates.

A presentation of trace element variations observed at the sampling depth ranges for each mine are shown in Figures 15, 16, 17, and 18. It appears that larger trace element concentrations in Mine C-I occur in the upper two-thirds of the seam. For Mine C-II, it appears that the higher concentrations of elements occur in the surface of the seam. Element concentrations are slightly higher in the mid-seam area of Mine C-III. The seam depth variations for Mine C-IV show a general trend toward higher concentrations at the lower seam depths. On the basis of

TABLE 7

COMPARISON OF SINGLE SAMPLE TO COMPOSITE SAMPLE
FROM THREE LOCATIONS WITHIN COAL SEAM.
MINE C-I (1975)

Element ^{1/}	Surface		Mid-Seam		Base	
	Comp.	Single	Comp.	Single	Comp.	Single
As	1.8	7.6	3.5	3.5	1.3	3.5
Be	1.5	1.0	1.0	1.0	0.2	< 0.10
Cd	0.13	0.13	0.13	0.13	0.13	< 0.10
Cr	2.9	0.67	2.9	1.3	0.51	0.67
Cu	1.8	0.77	7.7	0.77	0.77	0.77
F	15.0	9.0	13.0	9.8	7.4	7.6
Pb	0.13	0.26	0.26	0.39	< 0.10	0.13
Hg	0.02	0.04	0.02	< 0.02	< 0.02	< 0.02
Mo	1.5	1.7	1.17	1.7	1.7	1.5
Ni	0.35	0.35	0.35	0.7	0.30	0.58
Se	< 0.18	0.22	0.50	0.44	< 0.18	< 0.18
U	0.33	0.33	1.2	0.14	0.25	0.25
V	4.1	0.82	4.1	1.80	1.8	0.82
Zn	1.2	1.2	2.5	1.1	0.53	1.1
S ^{2/}	0.74	0.73	0.53	0.64	0.60	0.57

^{1/} Concentration in micrograms per gram.

^{2/} Concentration percent by weight total sulfur.

TABLE 8

COMPARISON OF SINGLE SAMPLE TO COMPOSITE SAMPLE
FROM THREE LOCATIONS WITHIN COAL SEAM.
MINE C-II (1975)

Element ^{1/}	Surface		Mid-Seam		Base	
	Comp.	Single	Comp.	Single	Comp.	Single
As	3.5	3.5	< 0.54	3.5	0.76	1.5
Be	2.0	0.38	0.20	0.38	1.0	4.3
Cd	0.13	0.13	< 0.10	0.13	0.13	< 0.10
Cr	2.5	0.67	0.67	1.3	0.67	0.51
Cu	7.7	1.8	1.8	3.6	1.8	1.8
F	25.0	20.0	18.0	18.0	20.0	14.0
Pb	0.19	0.26	0.10	0.11	0.26	0.13
Hg	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Mo	1.7	1.7	1.5	2.9	1.7	1.7
Ni	5.8	1.5	0.7	3.5	0.7	1.3
Se	0.44	0.25	0.58	< 0.18	0.44	< 0.18
U	0.33	0.33	0.33	0.14	0.33	0.16
V	8.2	1.8	1.2	1.8	1.8	1.8
Zn	2.5	0.93	2.5	2.5	2.1	4.7
S ^{2/}	0.97	0.88	0.65	1.13	0.55	0.54

^{1/} Concentration in micrograms per gram.

^{2/} Concentration percent by weight total sulfur.

TABLE 9

COMPARISON OF SINGLE SAMPLE TO COMPOSITE SAMPLE
FROM THREE LOCATIONS WITHIN COAL SEAM.
MINE C-III (1976)

Element ^{1/}	Surface		Mid-Seam		Base	
	Comp.	Single	Comp.	Single	Comp.	Single
As	< 0.54	< 0.54	1.8	1.8	< 0.54	0.59
Be	0.10	< 0.10	0.20	0.10	0.10	< 0.10
Cd	0.11	0.13	0.27	0.13	0.11	0.13
Cr	0.25	0.67	1.0	0.51	0.22	0.58
Cu	0.68	2.7	3.6	1.4	0.60	3.6
F	11.0	11.0	13.0	11.0	13.0	11.0
Pb	0.26	0.19	0.19	0.19	0.10	0.51
Hg	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Mo	1.7	5.8	1.7	1.7	1.2	3.9
Ni	1.5	0.15	0.30	0.7	0.15	0.26
Se	0.18	< 0.18	< 0.18	0.58	< 0.18	0.22
U	0.11	0.28	0.65	0.33	0.14	0.33
V	0.82	4.1	4.1	1.8	0.82	3.1
Zn	2.1	1.2	1.1	12.0	0.30	2.5
S ^{2/}	0.56	0.50	0.63	0.71	0.61	0.68

^{1/} Concentration in micrograms per gram.

^{2/} Concentration percent by weight total sulfur.

FIGURE 15

COMPARISON OF TRACE ELEMENT CONCENTRATIONS AT VARIOUS SEAM DEPTHS, MINE C-I

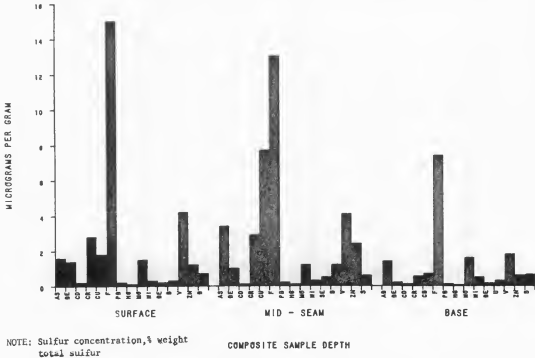


FIGURE 16

COMPARISON OF TRACE ELEMENT CONCENTRATIONS AT VARIOUS SEAM DEPTHS, MINE C-II

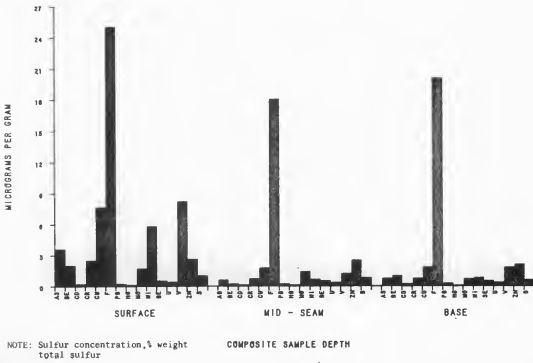


FIGURE 17

COMPARISON OF TRACE ELEMENT CONCENTRATIONS AT VARIOUS SEAM DEPTHS, MINE C-III

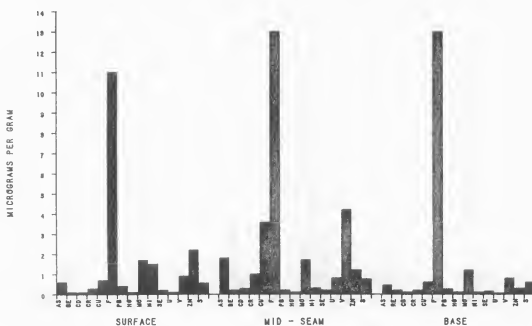
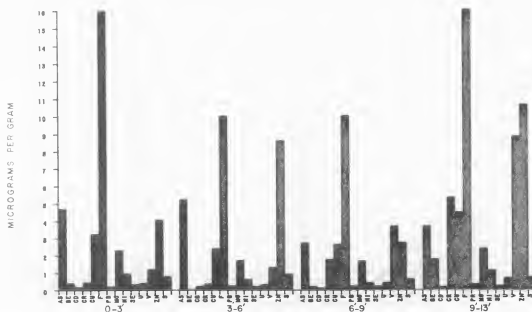


FIGURE 18

COMPARISON OF TRACE ELEMENT CONCENTRATIONS AT VARIOUS SEAM DEPTHS, MINE C-IV



the total number of samples analyzed, it appears that trace element chemical relationships vary from mine to mine and within seam depths within specific mines. Tables 7, 8, and 9, also show that the trace element concentrations vary with seam depth.

The focus of coal sample collection was to obtain data for use in the calculation of trace element emissions for energy conversion facilities in the study area. The emission rates for each trace element were obtained from the mine specific coal concentrations and feed rates for each of the specific energy conversion facilities. An exception in the emission rate calculations involved Facility P-VI which is no longer in operation. The trace element concentrations for the feed coal in this case were arbitrarily selected from the coal data from Mine C-III, as shown in Table 10, since the coal source for Facility P-VI no longer exists.

Soils

The geochemical maps presented in Figures 19a through 19k display the extractable trace element concentrations, as determined by analysis of soil samples in the sampling grid. These maps show chemical distributions for the eleven elements arsenic, beryllium, cadmium, chromium, copper, lead, nickel, sulfur, uranium, vanadium, and zinc. Although the magnitude of these trace elements varies only by a factor of four within the sampling area, there does appear to be a relationship of the higher concentrations to the lignite coal-fired facilities.

TABLE 10

AVERAGE TRACE ELEMENT CONCENTRATIONS FROM
ALL COMPOSITE SAMPLES FROM EACH MINE STUDIED

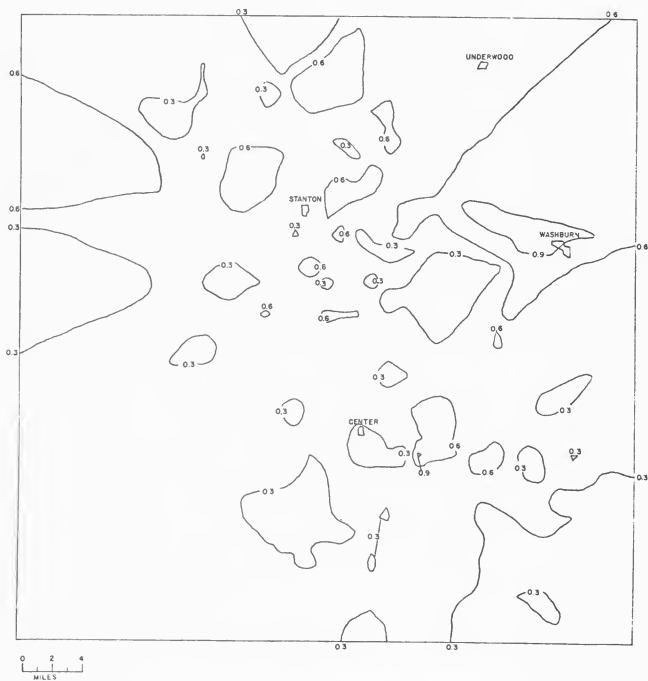
Element ^{1/}	Coal Mine				Arithmetic Mean
	C-I	C-II	C-III	C-IV	
As	2.2	1.60	0.96	3.5	2.07
Be	0.9	1.06	0.17	0.86	0.75
Cd	0.13	0.12	0.16	0.11	0.13
Cr	2.10	1.28	0.49	1.3	1.29
Cu	3.42	3.77	1.63	2.7	2.88
F	11.8	21.0	12.33	17.0	15.53
Pb	0.16	0.18	0.18	0.51	0.26
Hg	0.02	< 0.02	< 0.02	0.09	<u>3/</u>
Mo	1.46	1.63	1.53	1.9	1.63
Ni	0.33	2.40	0.65	0.35	0.93
Se	0.29	0.49	0.18	0.22	0.30
U	0.59	0.33	0.30	0.65	0.47
V	3.33	3.73	1.91	1.8	2.69
Zn	1.41	2.37	1.17	5.3	2.56
S ^{2/}	0.62	0.72	0.60	0.95	0.72

1/ Concentration in micrograms per gram.

2/ Concentration percent by weight.

3/ Greater than 30% of samples less than detectable limit,
resulting in arithmetic mean of <0.02.

FIGURE 19a
GEOCHEMICAL MAP OF ARSENIC



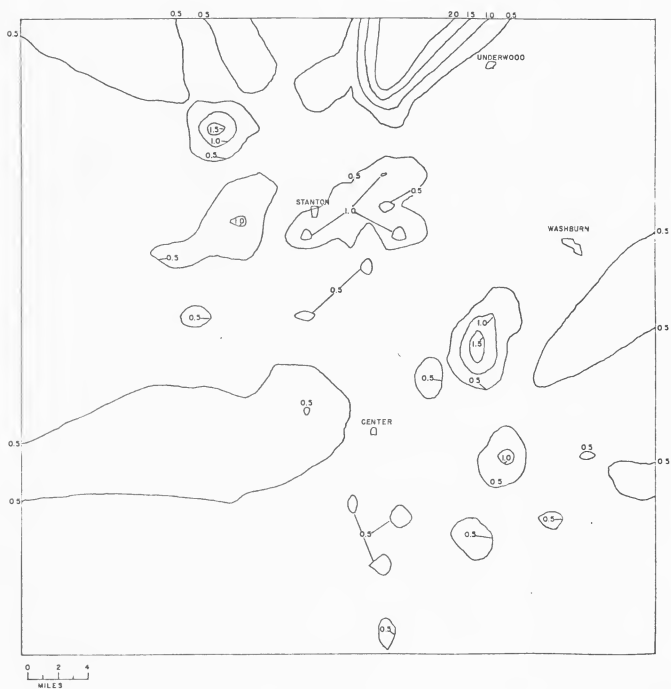
NOTE: isoline concentrarions in micrograms per gram

FIGURE 19b
GEOCHEMICAL MAP OF BERYLLIUM



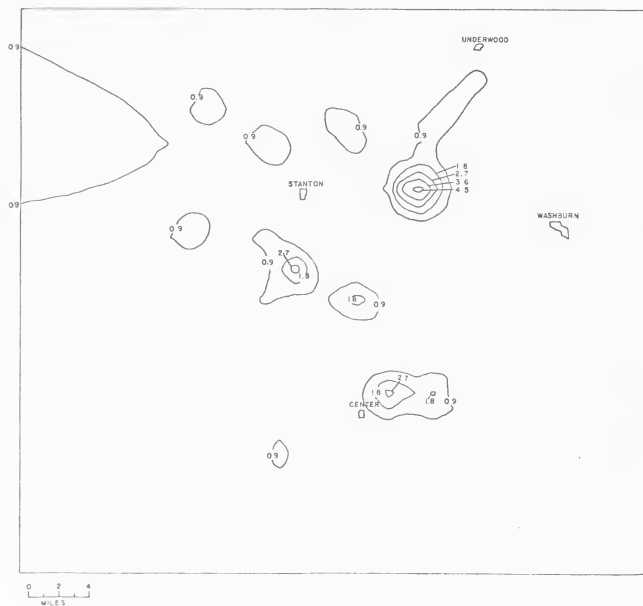
NOTE: isoline concentrations in micrograms per gram

FIGURE 19c
GEOCHEMICAL MAP OF CADMIUM



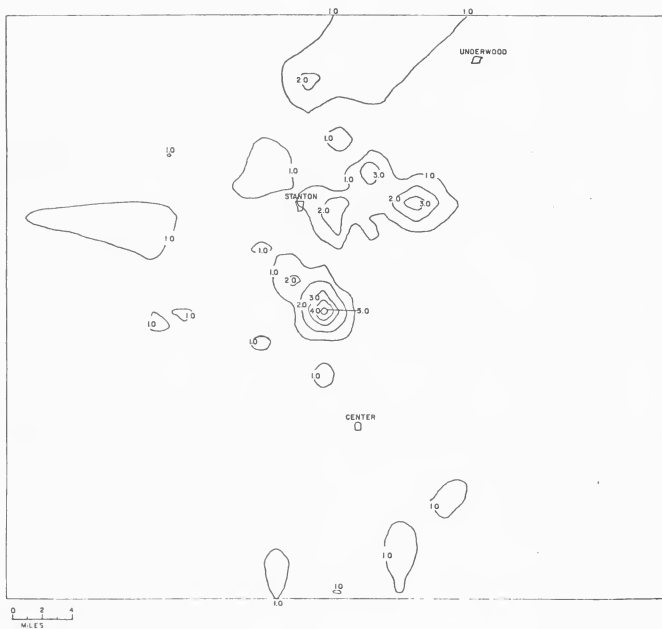
NOTE: isoline concentrations in micrograms per gram

FIGURE 19d
GEOCHEMICAL MAP OF CHROMIUM



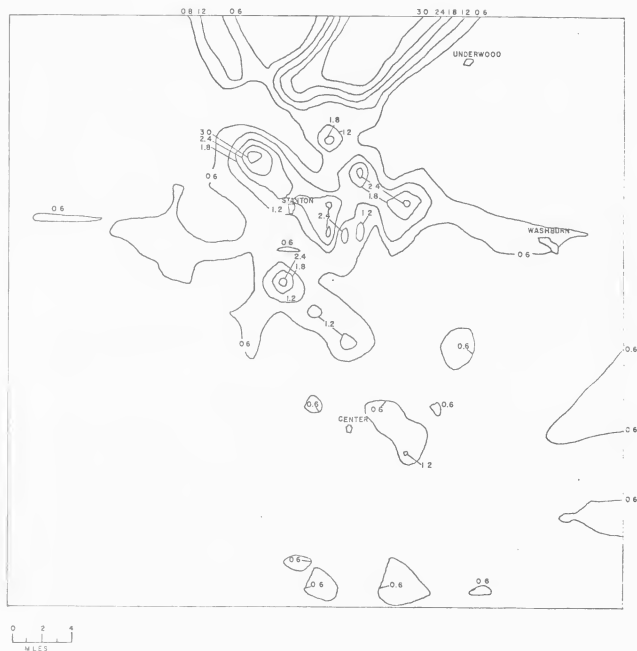
NOTE: isoline concentrations in micrograms per gram

FIGURE 19e
GEOCHEMICAL MAP OF COPPER



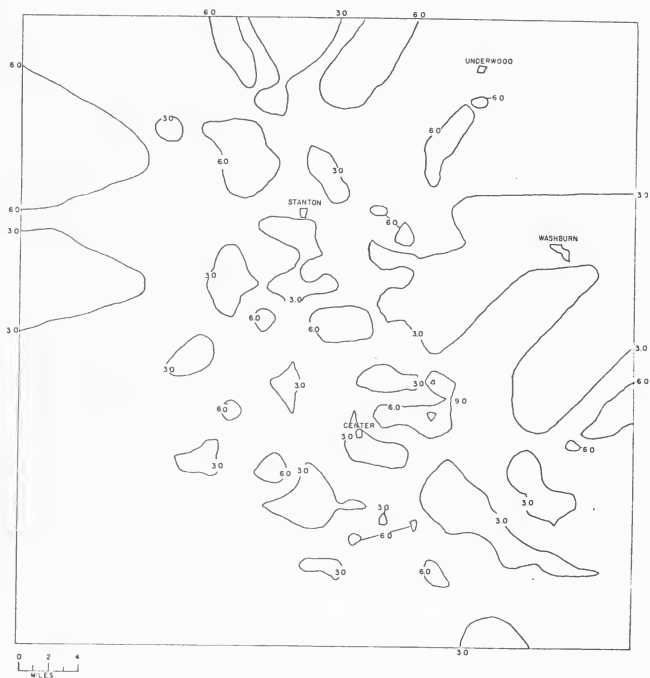
NOTE: isoline concentrations in micrograms per gram

FIGURE 19f
GEOCHEMICAL MAP OF LEAD



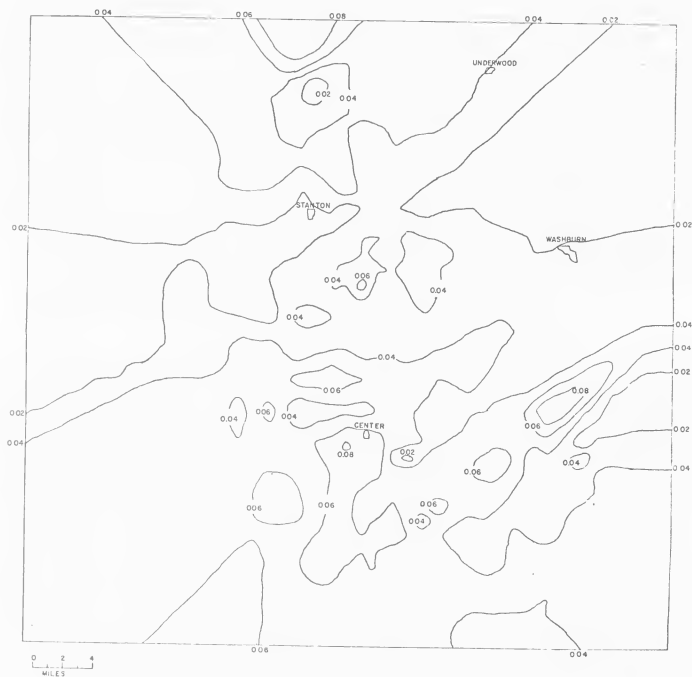
NOTE: isoline concentrations in micrograms per gram

FIGURE 19g
GEOCHEMICAL MAP OF NICKEL



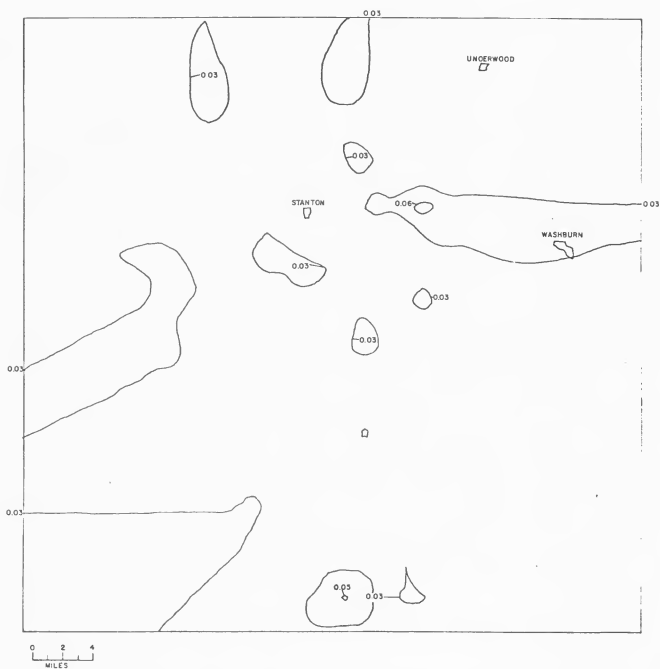
NOTE: isoline concentrations in micrograms per gram

FIGURE 19h
GEOCHEMICAL MAP OF SULFUR



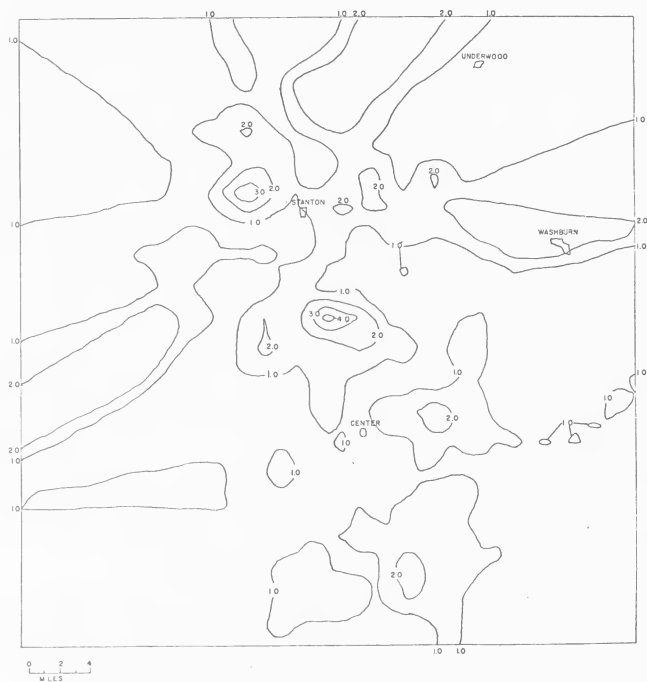
NOTE: isoline concentrations as total sulfur, % weight

FIGURE 19i
GEOCHEMICAL MAP OF URANIUM



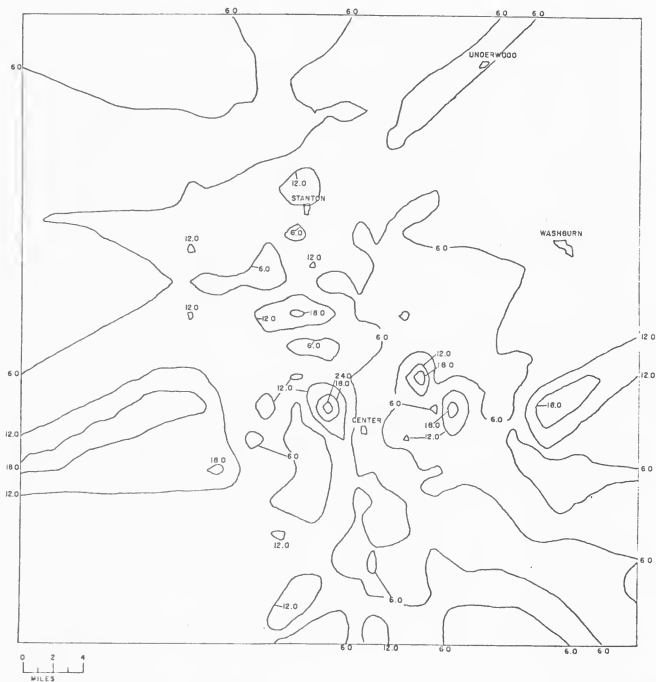
NOTE: isoline concentrations in micrograms per gram

FIGURE 19j
GEOCHEMICAL MAP OF VANADIUM



NOTE: isoline concentrations in micrograms per gram

FIGURE 19k
GEOCHEMICAL MAP OF ZINC



NOTE: isoline concentrations in micrograms per gram

Positive correlation of the higher trace element concentrations shown on these maps to the integrated emissions from the respective facilities could not be undertaken within the limited scope of this phase of study.

Intensifying the soil sampling grid around the respective facilities, (Figure 9a), and comparisons with specific trace element deposition patterns over the study area will be considered in the next phase of this study. Nevertheless it is possible that the underlying parent soil material and various geological formations of the study area may account for the geochemical variations displayed on these maps. In any event the concentration variations could not be definitely attributed in this phase of study to existing operating energy conversion facilities in the study area.

The evaluation of trace elements in soils involved the comparison of trace elements in cultivated soil to those in undisturbed soils. The purpose of this comparison was to assess the influence of agricultural activities on trace element concentrations. The arithmetic mean concentrations for samples of cultivated field and corresponding undisturbed soils are presented in Table 11. One standard deviation of sample variance was calculated for each element for all cultivated field soil samples. A statistically significant difference between the undisturbed and cultivated soils was determined to occur when the difference between the arithmetic mean of the

TABLE 11
RELATIONSHIP OF CULTIVATED FIELD SOIL TRACE ELEMENT
CONCENTRATIONS TO UNDISTURBED SOIL CONCENTRATIONS

Element	Undisturbed Soils ^{1/}	Cultivated Soils ^{1/}	Standard Deviation Cultivated Soils
Arsenic	0.49	0.43	±0.16
Beryllium	0.25	0.24	±0.06
Cadmium	0.54	0.40	±0.14
Copper	0.79	0.70	±0.30
Chromium	0.60	0.34	±0.19
Nickel	4.8	5.0	±1.62
Vanadium	1.26	0.79	±0.20
Zinc	7.6	3.6	±1.3

^{1/} Arithmetic mean of extractable concentrations in micrograms/gram

undisturbed soil and the corresponding cultivated soil was more than one standard deviation. A significant difference in concentrations can be observed to exist only between the soil groups for the elements chromium, vanadium, and zinc.

Data is presented in the analysis for only eight of the fifteen elements under consideration. A major portion of analytical data for the elements lead, mercury, molybdenum, selenium, and uranium, were found to be at concentration values below the quantifiable detectable limit. Also, no analytical data for sulfur and fluoride is available for cultivated field soil samples. For the elements arsenic, beryllium, cadmium, copper, and nickel, the observed differences between the two corresponding types of samples were not considered significant.

Chromium, vanadium, and zinc concentrations in undisturbed soils, are greater than the cultivated field soil concentrations plus one standard deviation. The influence of agricultural activities, such as tillage, crop types, crop rotation, and fertilizer practices cannot be ignored in evaluating trace element anomalies of significance relative to the "natural" geochemical trace element levels observed in undisturbed soils.

Cultivated soils were also collected as profile samples to determine whether significant geochemical variation in element concentrations exist with increasing depth in the upper level of root zones for food and forage crops. Data concerning trace

element concentrations in these profile samples is shown in Table 12. This data demonstrates insignificant concentration differences at the depth ranges presented.

Thirty-five soil profile samples were collected from undisturbed soils for assessment of the soil trace element concentrations through three depth ranges. The arithmetic mean concentration for each element for various sampling depths are presented in Table 13. Only eight of the fifteen elements in this study are presented in this table. The arithmetic mean concentrations for mercury, lead, uranium, molybdenum, and selenium were not calculated since greater than 30 percent of the analytical values obtained were less than the quantifiable detectable limit. Also, complete profile analysis for fluoride and sulfur content was not performed in the course of this study. From Table 13, it can be observed that all of the trace elements were found to have a uniform concentration in the depth range from 0 to 9 inches.

Deposition Patterns for Specific Facilities

Trace element deposition patterns for each of the six facilities were computer projected using the facility and coal data shown on Tables 5 and 10, respectively. Feed coals for facilities P-I, P-II, P-III, P-IV, and P-V were Mines C-IV, C-III, C-III, C-II, and C-I, respectively. The joint frequency wind data used for this analysis was derived from wind observations taken by the the National Weather Service Office at Bismarck, North

TABLE 12
ELEMENT CONCENTRATIONS AT TWO DEPTH RANGES FOR
CULTIVATED FIELD SOIL SAMPLES

Element	Depth Range and Concentration ^{1/}		Standard Deviation 0-4" Samples
	0-4"	4-8"	
Arsenic	0.43	0.39	±0.17
Beryllium	0.25	0.25	±0.08
Cadmium	0.38	0.35	±0.14
Chromium	0.37	0.37	±0.17
Copper	0.70	0.62	±0.31
Nickel	5.0	4.15	±1.57
Vanadium	0.79	1.12	±0.21
Zinc	3.61	3.11	±1.30

^{1/} Arithmetic mean of extractable concentrations in micrograms per gram.

TABLE 13
TRACE ELEMENT CONCENTRATIONS
IN PROFILE SAMPLES OF UNDISTURBED SOILS
(1975)

Element	Depth ^{1/}			Standard Deviation 0-3" Samples
	0-3"	3-6"	6-9"	
Arsenic	0.41	0.39	0.38	±0.16
Beryllium	0.20	0.22	0.21	±0.13
Cadmium	0.38	0.36	0.41	±0.25
Chromium	0.56	0.40	0.50	±0.41
Copper	0.69	0.76	0.97	±0.53
Nickel	4.89	3.62	4.93	±5.90
Vanadium	1.25	0.94	1.11	±0.97
Zinc	6.83	3.52	3.45	±4.48

^{1/} Arithmetic mean of extractable concentrations in micrograms per gram.

Dakota and represents an annual climatic average condition for years 1948 to 1974.

The shape of a deposition pattern around a facility stack is primarily dependent upon the frequency of occurrences of wind direction and speed, and stack height. The magnitude of deposition at a given location depends upon the trace element emission rate from the stack, particle size of the stack effluent, and the downstream distance of the location from the stack. Figures 20 and 21 display annual deposition patterns for selenium from Plants P-V and P-VI, respectively.

The choice of selenium for this analysis was arbitrary, and does not imply that this element is more or less environmentally hazardous. Such an analysis remains for subsequent study efforts. Deposition patterns for other trace element emissions from these two facilities would have the same shapes; the magnitudes can be obtained by dividing the emission rates for these elements from equation (7) by the emission rate for selenium as presented in the Methods section of this report.

In Figure 20, the maximum deposition occurs to the east-southeast through southeast of the facility stack. This is caused by the higher (relative to other directions) occurrence of winds from the northwest. A secondary maximum anomaly (regions of high deposition relative to surrounding regions) in Figure 20 occurs northward of the facility stacks. These

FIGURE 21

SELENIUM DEPOSITION FOR FACILITY P-VI IN UNITS OF $\mu\text{g}/\text{m}^2/\text{yr}$



anomalies are not as evident in Figure 21, although the same wind data was used; the reason is due to a much shorter stack and larger diameter of emission particles for Facility P-VI.

Facility P-V can be characterized as a "contemporary" facility in that its features are representative of recent coal-fired facility design and operation. Facility P-VI can be characterized as a "historic" facility in that its features are representative of early coal-fired power plant design and operation. Table 14 demonstrates a qualitative comparison of "contemporary" and "historic" facilities.

The numerical modeling analysis has identified a significant facility performance difference. This difference is a reduction in deposition with improved emission control systems. The improvements in facility design and operation are shown by this analysis to have reduced the ratios of deposition per unit of power generation by a factor of about 1000. In the relative comparison of facility designs, historic facility designs are those of the mid-1920's, while contemporary designs represent the engineering technology of the mid-1960's.

A "typical" design schematic for the inlet and outlet stream flows of new facilities of the design scheme of the mid-1970's is shown in Figures 22a and 22b. The marked advances in new facility design and emission control equipment technology, when compared to the older facility design schematics, is quite

TABLE 14
A RELATIVE COMPARISON OF TWO FACILITY DESIGNS

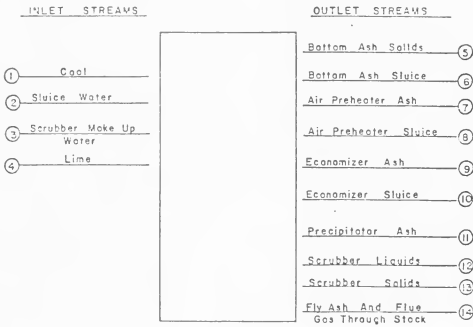
DESIGN	HISTORIC ^{1/} DESIGN	CONTEMPORARY ^{2/} DESIGN	APPROXIMATE DIFFERENCE
Stack height	low	high	factor of two
Coal feed rate	low	high	factor of fifteen
Emissions control	no	yes	
Power generation	low	high	factor of twenty
Point of maximum deposition	less than 5 kilometers from the stack	more than 10 kilometers from the stack	
Maximum annual deposition	very high	low	factor of fifty
Maximum annual deposition per unit of power generation	very high	low	factor of one thousand

^{1/} Approximate design period 1920

^{2/} Approximate design period 1960

FIGURE 22a

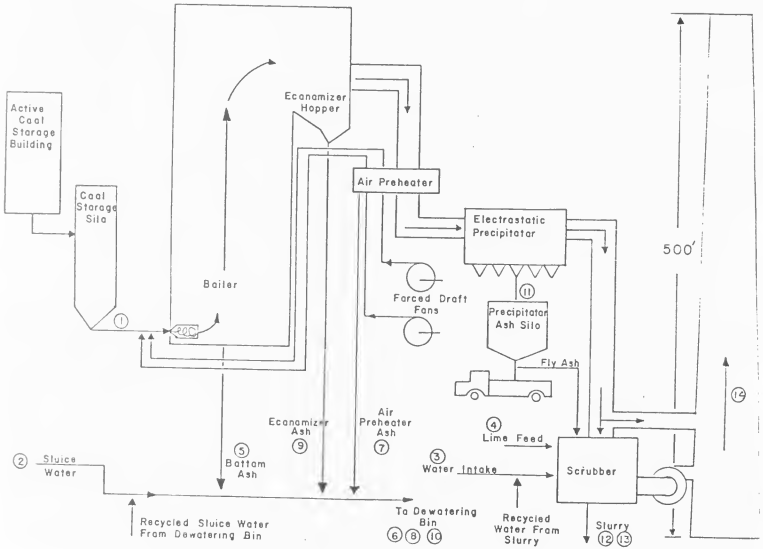
INLET AND OUTLET STREAMS
TYPICAL OF NEW AND PROPOSED
FACILITIES IN THE STUDY AREA



SOURCE: Radian Corporation 1975

FIGURE 22b

TYPICAL DESIGN OF NEW AND PROPOSED FACILITIES
IN THE STUDY AREA



SOURCE: Radian Corporation 1975

evident. In general, the new facilities have incorporated within their design schemes electrostatic precipitators for fly ash control and lime supplemented and other scrubber systems for sulfur dioxide control.

A composite trace element deposition pattern for all facilities in the study area was also performed by computer analysis. The surface deposition in the study area becomes an accumulation of the depositions from each of the six facilities influencing the area. An assessment of the net impact can be made from an area-wide analysis which includes all of these facilities.

Figure 23 displays the numerical dispersion model projections of annual trace element deposition of selenium for those plants currently operating (P-I, P-II, P-III, P-IV, and P-V); while Figure 24 also includes Facility P-VI which has not operated since 1969. These figures were obtained by placing the individual plant deposition patterns in proper geographic perspective and integrating the individual patterns into an accumulation of deposition for the area.

In Figures 20 and 21, anomalies occur near the facility stack, north of the stack, or southeast of the stack. The anomaly north of Facility P-I and southeast of Facilities P-III and P-IV in Figure 23 is caused by the interaction of these three facilities. As observed by comparison of Figures 20 and 21, the projected deposition for Facility P-VI is nearly ten orders of

FIGURE 23

COMPOSITE SELENIUM DEPOSITION WITHIN THE STUDY AREA
FROM FACILITIES P-I, P-II, P-III, P-IV AND P-V IN $\mu\text{g}/\text{m}^2/\text{yr}$

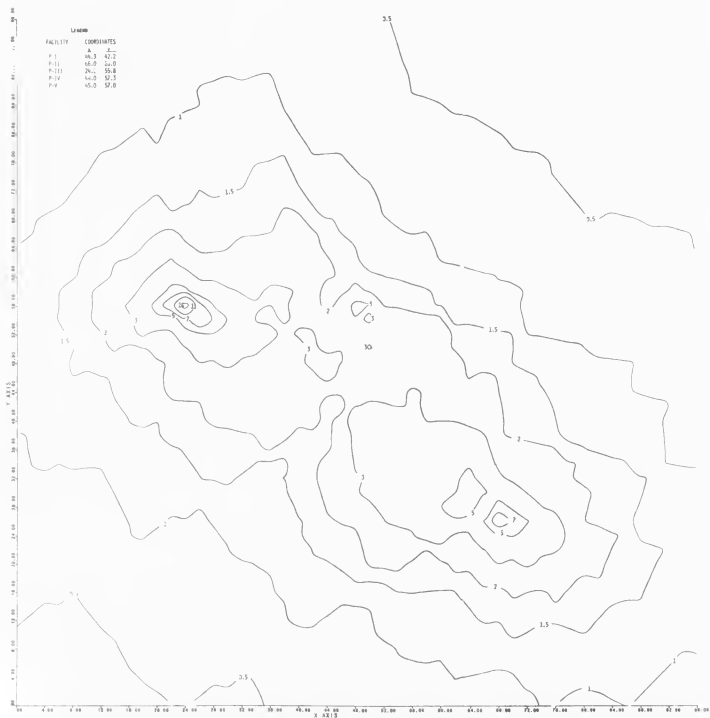
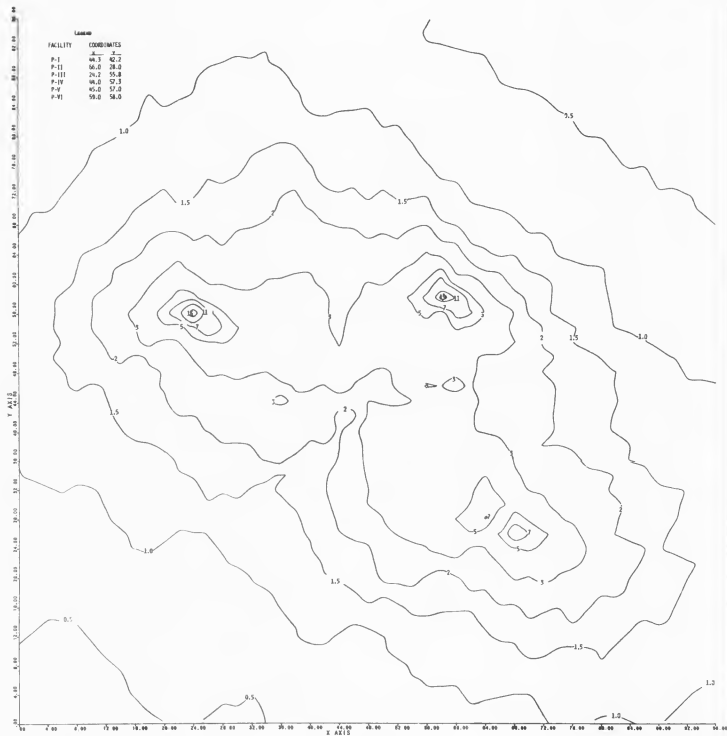


FIGURE 24

COMPOSITE SELENIUM DEPOSITION WITHIN THE STUDY AREA
FROM THE SIX COAL-FIRED FACILITIES IN $\mu\text{g}/\text{m}^2/\text{yr}$



magnitude greater than Facility P-V. Figure 24, when compared to Figure 23, demonstrates the overriding influence of Facility P-VI within a 50 kilometer (km) radius around this facility prior to 1969.

The surface deposition of a trace element has many facets which must be inventoried; for example, some of the trace element falls on leaves of plants and is taken into the plant through leaf surfaces, some is filtered downward through the soil surface, some is relocated by wind and water erosion, and so forth.

A perspective of the magnitude of projected deposition in relationship to the soil concentration of a trace element is demonstrated below. Consider a "worst" case situation from Figure 24 in which the annual deposition occurs directly on the soil surface and remains on the surface in an extractable form. A typical soil density of 1.5 grams per cubic centimeter (gm/cm^3) is equal to 1 gram per 0.67 cubic centimeters ($\text{gm}/0.67 \text{ cm}^3$). A cube of 0.67 has a surface area of 0.76 square centimeters (cm^2) and a depth of 0.87 centimeters (cm). In Figure 24, the maximum deposition is 19.15 micrograms per square meter per year ($\mu\text{g}/\text{m}^2/\text{yr}$), which is equivalent to 0.00146 micrograms per 0.76 square centimeters per year ($\mu\text{g}/0.76 \text{ cm}^2/\text{yr}$). In this "worst case" situation, the annual soil enrichment per gram of surface soil is therefore 1.46×10^{-3} micrograms.

Table 6 lists the average selenium extractable soil concentration in surface samples as <0.20 micrograms per gram ($\mu\text{g/gm}$). Considering the surface concentration as 0.20 micrograms per gram ($\mu\text{g/gm}$), the "worst case" soil enrichment of 1.46×10^{-3} micrograms per gram ($\mu\text{g/gm}$) is 0.72% of the measured extractable soil concentration at that location. The relatively low annual rate of deposition does not imply insignificant impacts on available soil nutrients to plants, direct leaf uptake, wind and water erosion concentration in localized areas, or to animal and human health. These impacts must be placed into a perspective relative to existing exposure of living organisms to trace elements. The nature of any potential impacts will be addressed during continuing phases of this project.

CONCLUSIONS

This investigation of trace elements was designed and directed toward the achievement of five specific objectives. These objectives are: to identify potential-problem trace elements in coal, to determine the trace element profile of soils, to determine the rate and concentration build-up of trace elements in the soil reservoir from existing coal-fired power plants, to determine by dispersion modeling of air emissions the projected soil reservoir build-up of trace elements, and to examine the need for development of specialized control procedures for the trace element wastes from energy conversion facilities.

The identification of potential problem trace elements in coal ultimately rests with the dispersion and deposition of those elements to the environment through a translocation process involving the energy conversion of coal. In order to identify specific elements which may be producing or eventually produce adverse environmental effects, it is necessary to develop base data on the concentrations of each element in coal, their distribution by type of coal being utilized, and emission concentrations as a result of combustion processes.

The concentrations of fifteen specific trace elements in lignite coal were examined. These fifteen elements found in coal represent many of the trace elements which, when enriched in the

environment, present the potential for environmental impacts upon the biological components of a given ecosystem.

The analysis of the data has shown the trace element chemical relationships in coal to vary from mine to mine and within the coal beds of a given mine. On the basis of this information, the identification of potential-problem trace elements in coals must be approached from consideration of multiple coal analysis at a given mine in order to realistically evaluate the fate of these elements within a specific combustion process and the resulting emission concentrations dispersed and deposited over the surrounding environment.

In the course of examining the trace element enrichment of soils by atmospheric deposition, a comparison was made of relative differences in deposition rates between a coal-fired electrical generating facility designed in the 1920's and one designed in the 1960's. Although the more contemporary design used 15 times more coal than the facility designed in the 1920's, the maximum annual deposition rate attributed to the contemporary design was 1/50th of that of the smaller, 1920 facility. In consideration of maximum annual deposition rate per unit of electrical generation, the 1960 facility was found to be one thousandth of the rate for the facility which was designed in the 1920's.

There is a tendency to equate size of facilities with potential problems, the larger the facility the greater the problem.

Historical problems of pollution are not directly transferable without taking into account increased control of emissions, increased operating efficiencies and improvements in other design parameters. Although facility size and the magnitude of coal utilization are important considerations in environmental protection decisions, smaller is not necessarily better. The degree of emission control, dispersion characteristics of the facilities and interactions of multiple facilities are the major factors which must be considered in the decision-making process concerning the siting of energy conversion facilities.

The fate of trace elements within the combustion process of coal-fired electrical generating facilities could not be evaluated since such research was outside of the scope of this investigation. However, research efforts have been performed on the subject of trace element flows and mass balances in the combustion process. This information was evaluated to provide a basis for the assumptions applied to the calculation of emission rates utilized in the projection of ground level trace element deposition in the study area.

A review of the literature (Kaakinen et al., 1975; Cuffe et al., 1964; Capes et al., 1974; Billings et al., 1973; Davidson et al., 1974; and Diehl et al., 1972) concerning trace element mass balance flows and emission rates from electrical generating facilities has served to highlight the factors to be weighed in establishing trace element emission rates. These factors

include the specific boiler configuration, operating temperatures, coal chemical composition, emission control device(s), and the lack of reliable analytical standards to be used in the analysis of trace elements in coal, fly ash, and flue gases. From the work of these investigators and others (Lee and von Lehmden 1973; Schulz et al., 1975), the establishment of trace element emission rates and resulting deposition projections must be based on process-specific trace element data within a specific geographical area in order to address the question of environmental significance of any trace element.

The projected deposition of trace elements from six existing lignite coal-fired electrical generating facilities was evaluated in the course of this study. Emission rates utilized in the determination of the deposition were established for each facility using applicable data specific to that facility.

Through the application of an emission rate for the element selenium, an annual soil deposition was obtained. The projection of the deposition was performed using a climatological dispersion model with a deposition function yielding results in micrograms per square meter per year. The deposition units were subsequently converted to micrograms per 0.76 square centimeters per year (surface area of the cubic volume of one gram of soil) for comparison of the annual deposition relative to the existing soil trace element levels. This analysis showed

the annual deposition for the element selenium to be a maximum of 0.72% of the measured extractable soil concentration in the study area. This percentage was determined by dividing the maximum annual deposition by the minimum detectable limit concentration for selenium. As previously stated in the discussion, the choice of the element selenium for presentation of this analysis was arbitrary and does not imply that this element is more or less environmentally hazardous than any of the other fourteen elements involved in this investigation.

Lee and von Lehmden, 1973, have established that trace elements such as arsenic, beryllium, cadmium, chromium, nickel, selenium, vanadium, and zinc, are being mobilized in the atmosphere in association with particles emitted from fossil fuel combustion. It has also been shown by these authors and others (Kaakinen et al., 1975; Davidson et al., 1974; and Natusch et al., 1974) that the specific concentration of many trace elements, most notably lead, cadmium, zinc, chromium, vanadium, nickel, and copper, increase with decreasing particle size in fly ash derived from coal combustion. Consequently, the highest trace element concentrations are found in small particles (less than 10 microns in diameter). Only a small fraction of the total fly ash mass has a particle diameter of less than 10 microns. Typical emission control efficiencies for these smaller particles are less than 85%. However, the fraction emitted could present a potential environmental hazard.

The significance of this analysis is that potentially adverse trace elements in coal can be identified through their deposition to the environment, and that a methodology is available for making such determinations. The methods developed and utilized for projection of deposition patterns in this study are transferable and may be applied to any conversion process throughout the region, but variations of coal and soil geochemical data as well as conversion processes dictate a requirement for site specific analysis.

The dispersion-deposition methodology identifies elements in coal which have potential for environmental significance when compared to existing element concentrations. However, in the final analysis, the environmental significance of trace element deposition can only be determined by examining the environmental effect of that deposition over time. The environmental significance of trace elements depends upon the projected soil reservoir deposition of trace element emissions, the rate over time that this deposition occurs, and finally the relationship of the deposition of a trace element to the existing environmental receptor concentrations. The possible environmental effects of exposures from trace elements were identified by an extensive review of the literature. A summary of this review is presented in Appendix C.

The determination of the environmental effect or potential hazard of a trace element when released to the environment must

be weighed in light of a number of factual considerations and variables. Many considerations are specific to individual elements while others are applicable to groups of elements. Other considerations are also specific to the particular component of the environment upon which the potential effect is to be assessed. For example, the physical and chemical properties of the element and its subsequent interactions in the effluent streams of energy conversion facilities are directly related to factors affecting the deposition quantities, availability to environmental receptors, and the toxicity to that receptor.

The subsequent movement of an element in the soil depends upon the element's chemical properties. A trace element, when deposited, may be in an insoluble form or complexed with insoluble soil materials and exhibit no mobility or detectable effect. The movement of the element in soluble form into the soil matrix is subject to element-specific factors such as the soil pH, moisture content, and geochemical nature of the existing matrix itself. (See Appendix C1) The movement of an element into the soil matrix becomes interrelated with subsequent uptake by vegetation and soil organisms.

Vegetation may be affected by trace element deposition along several pathways. These are direct deposition of the element on the above ground plant surfaces and absorption through the root systems. However, the concentrations required to cause adverse

effects through these pathways vary from element to element, and between species of plants, in addition to the nature of the chemical form of the element. (See Appendix C2)

The movements of trace elements through the environment are intricately interrelated through the soil, vegetation, and animal food chain links. (See Appendix C3 and C4) The complexities of trace element movement through the environment of living organisms are such that they could not be explored in depth within the limited scope of this investigation. Therefore, inference as to the effects of any one trace element or group of elements on the geochemical and biological components of the environment could not be formulated at this stage of study.

The deposition analysis presented for selenium showed the annual rate to be small in relationship to the concentrations found to exist in the soils throughout the study area. Annual depositions for the other fourteen elements under consideration can also be examined by application of the methodology established in this study.

On the basis of adverse response levels found in the literature (Appendix C), the projected depositions on environmental receptors calculated in this phase of research are not expected to cause adverse effects on ecosystems during the short-term period of one year. However, questions still remain relative to

the potential long-term effects of trace element emissions in the study area. These questions become of greater significance with a projected increase in coal utilization in the study area and the states of the Old West Region.

APPENDIX A

Trace Element Concentrations In Various Coals

Trace Element Concentrations in Various Coals

Arsenic:	Concentration	Reference
Percent in ash:	0.2%	Duck and Himes (1931)
Lignite percent in ash:	0.1 - 1.0%	Deul and Annell (1956)
Percent in ash:	0.8%	Stewart (1963)
All coals, average:	5.0 ppm	Bertine and Goldberg (1971)
Lignite, Center, ND	5.0 ppm	Ebasco Services, Inc. (1973)
Lignite, Stanton, ND	8.0 ppm	Basin Electric Power Cooperative (1972)
Lignite, Underwood, ND	6.4 ppm	Burns and McDonnell (1973)
Lignite	5.0 ppm	Federal Energy Admin. (1975)
Beryllium:		
Lignite: North Dakota	0.1 - 4.0 ppm	Stadnichenko (1961)
Sub-bituminous: Montana	0.1 - 9.1 ppm	
Sub-bituminous: Wyoming	0.1 - 0.7	
All types: average	3.0 ppm	Bertine & Goldberg (1971)
Lignite: North Dakota	0.23 ppm	North Dakota Geological Survey (1973)
Lignite: North Dakota	0.54 ppm	Burns & McDonnell (1973)
Coals: Central U.S.	0.64	Zubovic (1966)
Lignite coal: range	<0.1 - 8.2 ppm	Zubovic et al. (1961)
Lignite: Center, ND	2.0 ppm	Ebasco Services, Inc. (1973)
Lignite: Stanton, ND	0.58 - 2.6 ppm	Basin Electric (1972)
Lignite: Northern U.S.	0.3 - 30.0 ppm	Sondreal et al. (1968)
Coals: Central & Western U.S.	0.2 - 4 ppm	Ruch et al. (1974)
Lignite: Center, ND	0.60 ppm	Radian Corporation (1975)
Cadmium:		
U.S.: all types	0.2 - 10.0 ppm	Abernethy et al. (1969)
Bituminous coal from:		
Illinois and Kentucky:	1.0 - 2.0 ppm	Lagerwerff et al. (1970)
Lignite: Underwood, ND	0.01 ppm	Burns & McDonnell (1973)
Lignite: Center, ND	0.67 ppm	Ebasco Services, Inc. (1973)
Lignite: Stanton, ND	0.21 - 0.53 ppm	Basin Electric Coop. (1972)
General: Central & Western ND	0.10 - 65.0 ppm	Ruch et al. (1974)
Chromium:		
All Types: Average	10 ppm	Bertine & Goldberg (1971)
Lignite: Stanton, ND	77 ppm	Basin Electric (1972)
Lignite, Western ND	4.0 ppm	North Dakota Geological Survey (1973)
Coal, Central U.S.	12 ppm	Zubovic (1966)
Lignite, ND average:	7.5 ppm	Zubovic (1961)

Copper:	Concentration	Reference
Lignite: Western ND	1.70 ppm	North Dakota Geological Survey (1973)
Sub-bituminous: Montana	11 - 18.0 ppm	Dept. of Health and Env. Science (1976)
Lignite: Center, ND	10.5 ppm	Radian Corporation (1975)
	<1.0 - 45 ppm	Zubovic (1966)
Lignite ash: North Dakota	.001-.031 by wt/ash	Zubovic et al. (1961)
Lignite: Underwood, ND	16 ppm	Burns & McDonnell (1973)
Lignite: Stanton, ND	15 - 34 ppm	Basin Electric (1972)
	15 ppm	Bertine & Goldberg (1971)
All types: U.S.	5 - 61 ppm	Ruch et al. (1974)
	.0001-0.1% wt/ash	Deul & Annell (1956)
Lignite ash: ND	.025% wt/ash	Brewer & Ryerson (1935)
Lignite - sub-bituminous	58 - 3020 ppm	O'Gorman & Walker (1972)
Lead:		
U.S. Coals: average percent in ash:	0.01 - 0.13%	Abernethy & Gibson (1963)
Lignite coal: Center, ND	0.86 ppm	Radian Corporation (1975)
U.S. coals: average	25 ppm	Bertine & Goldberg (1971)
Poplar River coals: Montana range	11 - 27 ppm	Dept. of Health and Env. Science (1976)
Lignite: Western ND	2.70 ppm	North Dakota Geological Survey (1973)
Lignite: Underwood, ND average	0.5 ppm	Burns & McDonnell (1973)
Lignite: Center, ND	7.0 ppm	Ebasco Services (1973)
Lignite: Stanton, ND range	5.4 - 11 ppm	Basin Electric (1972)
Lignite and sub-bituminous: Average:	60 ppm	O'Gorman & Walker (1972)
Range:	20 - 165 ppm	
Lignite: in percent of ash	0.1 - 1.0%	Deul & Annell (1956)
All samples Central and Western United States	4.0 - 218.0 ppm	Ruch et al. (1974)
Mercury:		
U.S. coals: average range	0.5 - 3.3 ppm	Grant (1971)
U.S. sub-bituminous coal:	1 - 25 ppb	Joensuu (1971)
Central and Western U.S.:	0.02 - 1.60 ppm	Ruch et al. (1974)
Range (percent mercury in ash):	0.007 - 0.019%	Headlee & Hunter (1955)
Western coals (percent mercury in ash)	<0.10%	Deul & Annell (1956)
Lignite: Center, ND	0.074 ppm	Radian Corporation (1975)
Lignite: Center, ND	0.10 ppm	Ebasco Services, Inc. (1973)
Lignite: Stanton, ND	<0.20 ppm	Basin Electric (1972)
Lignite: Underwood, ND	0.094 ppm	Burns & McDonnell (1973)

Molybdenum:		Concentration	Reference
Samples: Central and Western U.S.		1 - 30 ppm	Ruch et al. (1974)
Lignite coal: North Dakota		1 - 100 ppm	Sondreal et al. (1968)
Coal average:		32 ppm	Abernethy (1969)
Coals, average:		1.5 ppm	Magee & Hall (1973)
Lignite: Stanton, ND		5.2 - 17.0 ppm	Basin Electric (1972)
Lignite: Western ND average		3.8 ppm	North Dakota Geological Survey (1973)
Lignite: ND average		0 - 12.8 ppm	Zubovic et al. (1961)
Nickel:			
Average concentration		15 ppm	Bertine and Goldberg (1971)
Range observed in coal ash:		3.0 - 10,000 ppm	Abernethy & Gibson (1963)
Central and Western U.S. coal average:		21 ppm	Ruch et al. (1974)
Range:		3.0 - 80.0 ppm	
Northern Great Plains lignites		10 - 300 ppm	Sondreal et al. (1968)
Lignite and sub-bituminous coals		20 - 420 ppm	O'Gorman & Walker (1972)
Lignite: ND average		1.90 ppm	North Dakota Geological Survey (1973)
Lignite: ND range		1.3 - 40.0 ppm	Zubovic et al. (1961)
Lignite: Center, ND		13 ppm	Ebasco Services, Inc. (1973)
Lignite: Stanton, ND		7.5 - 60.0 ppm	Basin Electric (1972)
Lignite: Center, ND		5.4 ppm	Radian Corporation (1975)
Selenium:			
U.S. coal samples			Pillay et al. (1969)
Average		3.2 ppm	
Range		0.46 - 10.65 ppm	
Lignite: Center, ND		1.3 ppm	Radian Corporation (1975)
Lignite: Stanton, ND		0.10 - 0.41 ppm	Basin Electric (1972)
Lignite: Center, ND		1.3 ppm	Ebasco Services (1973)
Coals from Central and Western U.S.:		2.08 ppm	Ruch et al. (1974)
Range:		0.45 - 7.70 ppm	
Vanadium:			
Range of vanadium concentrations for U.S. coals:		16 - 176 ppm	Athanasiadis (1969)
Lignite: Stanton, ND		0.23 - 1.7 ppm	Basin Electric (1972)
Lignite: Center, ND		28 ppm	Ebasco Services, Inc. (1973)
Lignite: North Dakota average		11 ppm	North Dakota Geological Survey (1973)
Lignites: North Dakota range		2.2 - 355 ppm	Zubovic et al. (1961)
Lignite and sub-bituminous			O'Gorman & Walker (1972)
Average:		125 ppm	
Range:		20 - 250 ppm	
United States coals average:		94 ppm	Abernethy (1969)
Central and Western U.S. coals			Ruch et al. (1974)
Average:		32.71 ppm	
Range:		11 - 78 ppm	

Zinc:	Concentration	Reference
Lignite: Stanton, ND	20 - 79 ppm	Basin Electric (1972)
Lignite: Center, ND	9.8 ppm	Ebasco Services, Inc. (1973)
Lignite: North Dakota average	2.90 ppm	North Dakota Geological Survey (1973)
Lignite: North Dakota range	0 - 1800 ppm	Zubovic et.al. (1961)
Montana, Poplar River Coal Project:	7 - 16 ppm	Dept. of Health and Env. Science (1976)
Lignite and sub-bituminous range:	50 - 320 ppm	O'Gorman & Walker (1972)
Average: all coals	50.0 ppm	Bertine & Goldberg (1971)
Fluoride:		
Lignite: Center, ND	112 ppm	Ebasco Services, Inc. (1973)
Lignite: Stanton, ND	100 - 670 ppm	Basin Electric (1972)
Coal: Central & Western U.S. Range:	25 - 143 ppm	Ruch et al. (1974)
Average:	60 ppm	
Coal: Eastern & Central U.S.	85 - 167	Churchill et al. (1948)
Lignite: Center, ND	57 ppm	Radian Corporation (1975)
Sulfur:		
Average sulfur content of U.S. coals:		DeCarlo et al. (1966)
Bituminous coal:	<0.7 - >4.0%	
Sub-bituminous coal:	<0.7 - 2.0%	
Lignite coal:	<0.7 - 1.5%	
Anthracite:	<0.7 - 2.5%	
Sulfur content of North Dakota lignite by County:		DeCarlo et al. (1966)
Adams:	0.8 - 1.0%	
Bowman:	0.8 - 1.0%	
Burke:	<0.7 - 0.7%	
Burleigh:	<0.7 - 0.7%	
Dunn:	<0.7 - 0.7%	
Grant:	0.8 - 1.0%	
Hettinger:	<0.7 - 0.7%	
McLean:	<0.7 - 0.7%	
Mercer:	0.8 - 1.0%	
Morton:	1.1 - 1.5%	
Oliver:	0.8 - 1.0%	
Stark:	<0.7 - 0.7%	
Ward:	<0.7 - 0.7%	
Williams:	<0.7 - 0.7%	
Total sulfur in North Dakota lignite by County and Mine:		Walker & Harner (1966)
County Mine		
Adams Arrowhead	1.07%	
Bowman Twin Buttes	0.90%	
Burke Bonsness	0.32%	
Burleigh Kincaid	0.46%	
Burleigh Burleigh	0.64%	
Mercer Indianhead	0.57%	
Morton Kamins	0.57%	
Williams Knife River	0.88%	
Ward Flesher	0.61%	
Williams (All mines)	0.25%	
Avoca	0.62%	
Ray	0.43%	
Standard	0.60%	
Williston View	0.45%	
Total sulfur content of lignite shows in average range of:	0.1 - 1.9%	Sondreal, E.A. et al. (1965)
Total sulfur content: Poplar River Project - Montana average:	0.9%	Dept. of Health and Env. Science (1976)
Total content of U.S. coals by State: (average)		Rohrman & Ludwig (1965)
Montana:	0.70%	
North Dakota:	0.81%	
South Dakota:	0.70%	
Wyoming:	0.61%	

APPENDIX B

Trace Element Concentrations In Soils

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Trace Element Concentrations in Soils

Arsenic:	Concentration	Reference
Normal virgin soils:	1.3 - 2.5 ppm	Headen (1910)
Orchard soils, Western U.S.:	5.0 - 102.0 ppm	Groaves (1913)
Orchard soils, Oregon	3.0 - 14.0 ppm	Jones and Hatch (1937)
Normal surface soils: U.S.:	0.4 - 41.0 ppm	Williams and Whetstone (1940)
Natural conc. range of arsenic in soils:	5.0 ppm	Hawkes and Webb (1962)
Normal conc. range in soils:	1.0 - 70.0 ppm	Stewart (1963)
Concentration range in soils:	0.3 - 40.0 ppm	Misra and Tiwari (1963)
Average arsenic conc. in soils:	6.0 ppm	Miesch and Huffman (1972)
Normal soils; United States:	1.0 - 97.0 ppm	Shacklette et al. (1974)
Total arsenic conc. range: all soils	0.0 - 500.0 ppm	Federal Energy Admin. (1975)
Beryllium:		
Earth's crust: average	6.0 ppm	Goldschmidt (1954)
Soils: average range	6.0 ppm 0.1 - 40 ppm	Bowen (1966)
Scottish soils:	<5.0 ppm	Swain and Mitchell (1960)
Cadmium:		
Average conc.: Earth's crust	0.15 - 0.20 ppm	Fleischer et al. (1974)
Uncontaminated soils: U.S.	<1.0 ppm	Shacklette et al. (1973)
	0.5 - 2.0 ppm	Miesch & Huffman (1972)
Uncontaminated soils: U.S.	0.01 - 0.7 ppm	Fulkerson et al. (1973)
Avg. conc.: Normal soils	0.06 ppm	Bowen (1966)
Non-polluted soils	0.01 - 7.0 ppm	Allaway (1968)
Non-polluted - background	0.5 ppm	Warren et al. (1971)
Field soil, unfertilized	0.55 - 2.45 ppm	Schroeder (1967)
fertilized	3.38 ppm	
Chromium:		
Soil: Average	5.0 - 1000 ppm	Swaine (1955)
Soils: U.S. average	1.0 - 250 ppm	Robinson (1914)
Soils: Average	100 ppm	Bowen (1966)
Topsoil: NJ & PA	12 - 51 ppm	Conner et al. (1957)
Copper:		
United States	10 - 40 ppm	Boar (1957)
	20 (average) ppm	Hodgson (1963)
	2 - 100 ppm	Allaway (1968)
United States average:	2.5 - 125 ppm	Shacklette (1970)
North Dakota Samples	<12 - >37 ppm	Shacklette (1970)

	Concentration	Reference
Atlantic Coastal Plain	5 - 27 ppm	Holmes (1943)
Central and Western U.S.	6 - 67 ppm	Holmes (1943)
Native Soil (U.S.)	10 - 200 ppm	Rutherford & Labanauskas (1966)
Atlantic Coastal Region	1 - 30 ppm	
	7 - 30 ppm	Pratt & Bradford (1953)
Michigan Soils	14 - 120 ppm	Lucas (1948)
Utah Soils	7.2 - 24.5 ppm	Greaves & Andersen (1936)
Lead:		
Normal uncontaminated soils	0.05 - 5.0 ppm	Brewer (1966)
Natural concentration range	2.0 - 200 ppm	N.R.C. (1972)
World-wide average:	16 ppm	Goldschmidt (1937)
Average concentration:	10.0 ppm	Bowen (1966)
Normal concentration range:	6 - 108 ppm	Wright (1955)
Mercury:		
Mercury concentrations found in various soil categories:		Klein (1972)
Residential soils:	0.07 - 1.10 ppm	
Agricultural soils:	0.09 - 0.11 ppm	
Industrial soils:	0.10 - 0.14 ppm	
Average concentration: all soils and rock	0.05 ppm	Grant (1971)
Soil concentration average: U.S.		Shacklette (1971)
Eastern U.S.:	96 ppb	
Western U.S.:	55 ppb	
Natural background concentration in Western U.S.:	100 ppb	Pierce et al. (1970)
Natural concentration range of mercury in soils:	30 - 300 ppb	Hawkes & Webb (1962)
Average concentration: rocks and soils	100 ppb	Hammond (1971)
Average concentration of mercury in the Earth's crust:	0.07 ppm	Vinogradov (1959)
Average abundance of mercury: Earth's crust	0.5 ppm	Goldschmidt (1934)
Average: natural soils	0.10 ppm	Wallace et al. (1971)
Molybdenum:		
Natural background concentrations:	0 - 0.5 ppm	Barshad (1948)
Average molybdenum content of soils:	2.5 ppm	Robinson & Alexander (1953)
Average molybdenum content: U.S. soils	0.6 - 3.5 ppm	Robinson et al. (1951)
Average molybdenum content (181 random samples):	1.33 ppm	Clark & Axley (1955)
Range:	0.13 - 13.54 ppm	
Normal random soil samples:	0.79 - 2.21 ppm	Purvis & Peterson (1956)
Samples of New Jersey soils:	0.80 - 3.3 ppm	Evans & Purvis (1951)
Normal soils: Scotland	0 - 2 ppm	Mitchell (1944)

	Concentration	Reference
Total molybdenum content of soils: range	1.0 - 3.0 ppm	Lear (1957)
Average concentration molybdenum in Earth's crust:	2.3 ppm	Goldschmidt (1954)
Normal background soil concentration:	0.1 - 5 ppm	Mitchell (1964)
Normal background soil concentration:	2.0 ppm	Bowen (1966)
Average concentration in U.S. soils:	3 ppm	Shacklette (1970)
Soil concentration: Canadian Atlantic coastal area	0.05 - 12.1 ppm	MacLean & Langille (1973)
Total molybdenum in soils:	0.2 - 5 ppm	Bould (1963)
Nickel:		
Normal concentration of nickel:		Swaine (1955)
Average:	100 ppm	
Normal range:	5 - 500 ppm	
Normal concentration of nickel: Eastern U.S.	2.5 - 40 ppm	Painter et al. (1953)
Normal background concentration: Southern California	8 - 100 ppm	Vanselow (1952)
Normal range of nickel: soils	>1 - 100 ppm	Rogers et al. (1933)
Average concentration: Earth's crust	80 ppm	Sandell (1943)
Total nickel in soils: range	10 - 40 ppm	Bear (1957)
Average concentration of nickel: Earth's crust	100 ppm	Goldschmidt (1954)
Normal concentration of nickel in soil:	40 ppm	Bowen (1966)
Selenium:		
Earth's crust, normal range	0.03 - 0.8 ppm	Fleischer (1953)
Earth's crust, average concentration:	0.09 ppm	Goldschmidt (1954)
Volcanic rocks, Western U.S.	2.0 ppm	Davidson & Powers (1959)
Normal concentration of soils:	0.1 - 2.0 ppm	Swaine (1955)
Limestone materials: SD	<3.0 ppm	Moxon et al. (1938)
Sedimentary rocks: SD	0.2 - 33.5 ppm	Lakin (1961)
Sedimentary rocks: Western U.S.	0.02 - 1,500 ppm	
Soils: Gregory County, SD	0.5 - 13 ppm	Byers (1935)
average:	4.5 ppm	
Seleniferous soils: Western U.S.	1 - 6 ppm	Byers et al. (1938)
Soil concentration range entire U.S.	0.1 - 4.32 ppm	Shacklette et al. (1974)
Vanadium:		
Normal soils range:	3 - 230 ppm	Pratt (1966)
Normal soil range:	20 - 500 ppm	Swaine (1955)

Zinc:	Concentration	Reference
Zinc concentration in the lithosphere	80 ppm	Goldschmidt (1954)
Range of zinc in normal soils:	10 - 300 ppm	Swaine (1955)
Range of zinc in normal soils:	20 - 200 ppm	Bear (1947)
Average concentration of zinc in normal soils:	58 ppm	Vinogradov (1959)
Average concentration of zinc in normal soils:	50 ppm	Bowen (1966)
Normal zinc concentration for soil profiles in various areas:		Holmes (1943)
Atlantic Coastal Plain:	13 - 31 ppm	
Wisconsin Soils Profiles:	61 - 79 ppm	
Iowa Soil Profiles:	48 - 72 ppm	
Kansas Soil Profiles:	58 - 81 ppm	
Mississippi Drainage Basin:	34 - 120 ppm	
Fluoride:		
Average concentration: Pennsylvania soils	240 ppm	Steinkoenig (1919)
Average concentration: Surface soils, U.S.	292 ppm	Robinson & Edington (1946)
Average concentration: Entire U.S.	180 ppm	Shacklette et.al. (1974)
Average: Western U.S.	250 ppm	
Average: Eastern U.S.	115 ppm	
All soils, average concentration:	100 - 300 ppm	Bear (1957)
All soils, average concentration:	200 ppm	Bowen (1966)
Average concentration: all soils	300 ppm	Goldschmidt (1954)
Range of concentration:	10 - 1000 ppm	Bould (1963)
Sulfur:		
Total sulfur, field soils - average:	0.01 - 0.05%	Starkey (1950)
Total sulfur, American soils - average:	0.01 - 0.06%	Greaves & Gardner (1929)
Total sulfur, topsoil - range:	0.008-0.136%	Jordan & Ensminger (1958)
average total sulfur:	0.045%	
Soil sulfate, average concentration:	0.01 - 0.02%	Barbier & Chabannes (1944)

APPENDIX C

The Effects of Selected Trace Elements On:

Soils Appendix C1

Vegetation. Appendix C2

Animal Nutrition and Health Appendix C3

Human Nutrition and Health Appendix C4

The Effects of Selected Trace Elements on Soils

Arsenic:	Concentration	Reference
Arsenic residues contaminating soils are usually quite stable and are dispersed by leaching.		Johnson and Hiltbold (1969)
Arsenates are relatively insoluble in soils, not lost by leaching and accumulate.		Bear (1957)
Chemistry of As in soils is similar to that of phosphorus. Absorption is related to free iron oxide with increasing absorption as free iron oxide content increases.		Jacobs et.al. (1970)
Arsenic contamination of soil shows low penetration with increasing soil depth.		Williams and Whetstone (1940)
Arsenic and phosphorus show similar soil chemistry and attempts to reduce arsenic solubility coincidently can decrease levels in available soil phosphorus.		Underwood (1962)
Cadmium:		
Cadmium becomes associated with soil organic matter and may be geochemically recycled similar to mercury.		Fleischer et al. (1974)
Cadmium appears to be mobile in the industrially contaminated soils and was found at higher than expected background concentrations at depths to 30 centimeters.		Kobayashi (1971)
Cadmium content of soil markedly affects the cadmium content of plant roots. The type of soil appears to affect the movement of cadmium into plant roots and shoots.		John et al. (1972)
Chromium:		
Chromium has been associated with infertility in the soil at concentrations of:	1000 - 3900 ppm	Robinson et al. (1935)
The application of phosphate to the soil has shown the effect of intensification to chromium toxicity symptoms in various plants.		Hunter & Vergnano (1953)
Chromium additions to soil appears to cause only slight reductions of plant yield at levels of:	2 ppm	DeKock (1956)
Soluble chromium added to soils is likely to revert to insoluble oxides and results in only a temporary increase in extractable soil chromium concentrations.		Sullivan (1969)
Copper:		
Additions of copper to the surface of peat soils may remain in the top two inches for at least six years.		Mitchell (1964)
Copper often accumulates in topsoil, strongly absorbed to silicate mineral surfaces or chelated by organic matter. Soil treatments and climatic conditions which tend		Lagerwerff (1967)

Concentration	Reference
to increase soil acidity can cause copper toxicity to occur in vegetation where previously no toxicity problem existed.	
Copper has a pH dependent interaction with soil and becomes very strongly bound and very difficult to leach out or extract.	Hodgson (1963)
Copper has a low mobility in soil and does not readily move through the soil profile.	
Copper applied to organic soils in the form of the cupric ion remains in the zone of placement. Copper is retained by the soil and provides long-term residual effects.	Lucas (1948)
Lead:	
Lead from industrial contamination or from decayed plant material appears to be immobilized in the topsoil. Lead becomes fixed with various anions in the soil surface. Soil profiles demonstrate the apparent lead accumulations in soil surfaces.	Rains (1971)
Lead applied to soil appears to become associated with surface plant roots. Applied soil lead does not appear to affect the absorption of Zn, Cu, Mn, Fe or phosphorus from the soil to plants.	Broyer et al. (1972)
The large additions of soluble lead salts to various soils appears to produce only small increases in the concentration of lead in the tops of plants.	Allaway (1968)
Very close correlations exist between the fertility of the soil and its microflora. The addition of 250 ppm lead in soil with a pH below 4.5 will cause considerable harm to microflora.	Schonbeck (1974)
Lead has been observed to be distributed throughout soil samples with surface soils being somewhat richer in lead than subsoils. Lead content in soil appears to decrease with increasing pH.	Filipovic (1961)
In an instance of airborne contamination of soil by lead, approximately 90% of the metal deposited was retained in the upper 15 cm of soil.	Buchauer (1973)
Under acid soil conditions, the amounts of lead taken up by plants appears to be reduced with the addition of phosphate or lime.	MacLean et al. (1969)
Mercury:	
When soil has been contaminated with mercury compounds, the application of lime-sulfur or of elemental sulfur has decreased the mercury availability to vegetation.	Lagerwerff (1967)

Concentration

Reference

Mercury, when deposited on the soil, is retained in the upper soil surface on aerated soils. Mercury is retained through a valence-type ionic absorption by organic and inorganic materials. Also, retention takes place because many of the mercury compounds in soil have low solubilities such as mercury as phosphate, carbonate, and sulfide complexes.

In anaerobic soil conditions, mercury is at least partially converted into soluble forms such as monomethyl or gaseous dimethyl mercury complexes.

Lagerwerff (1972)

Molybdenum:

The molybdenum status of soil and its pH appear to be the main determinants of the level in all plant species. Molybdenum is not readily absorbed from acid soils and liming of such soils will increase molybdenum uptake by plants. High molybdenum concentrations in plants is usually associated with alkaline soils.

Underwood (1962)

The molybdenum found in alkaline soils appears to be highly water soluble and by acidification of the soil, the water soluble molybdenum concentration can be greatly reduced.

Barshad (1948)

Molybdenum accumulation by forage plants appears to be affected by its concentration in neutral soil, by species of plant, and by the depth of the water table. Accumulation of molybdenum by plants is proportional to the amount of soluble molybdenum added to soil in a pH range of 4.7 - 7.5. Forage grown where the water table is near the soil surface contained more molybdenum than did vegetation where the depth of the water table is greater. In the study, the growth of alfalfa was retarded when soil concentration of water soluble molybdenum reached levels of:

1500 ppm

Jensen & Lesperance (1971)

Molybdenum added in soluble form to most soils is quickly precipitated and slowly converted to less soluble forms. Leaching is not likely to remove significant amounts of molybdenum through acidic soil profiles except possibly in very sandy soils.

Smith & Loeper (1969)

In acid soils, the application of molybdenum and the natural soil content of molybdenum does not appear to significantly affect the yield of soybeans, but in areas of alkaline soils, the application of molybdenum appears to increase plant concentrations and may reduce the crop yield.

de Nooy (1970)

Concentration	Reference
The uptake of molybdenum from soil by wheat appears to increase with the addition of nitrogen fertilizers. It appears that the increase uptake may be due to the nitrogen-producing nitric acid which brings more molybdenum into solution.	Mishra et al. (1970)
Excessive molybdenum levels from various areas of the world which appear in herbage appear to be associated with alkaline soils with unusually high amounts of total molybdenum. Under acid conditions relatively high concentrations of molybdenum may be present without uptake by plants of levels significant to produce toxicity in both vegetation and animals.	Davies (1956)
The sorption of molybdate by soils depends on pH and molybdenum concentration. The precipitation of the molybdate ion with the ferric ion shows that ferric molybdate has a very low solubility at acid pH. Molybdenum appears to be more readily absorbed by hydrous ferric oxide than by other soil colloids. The principle that lime makes more molybdenum available to plants is that the molybdenum ion is absorbed by soil ferric hydroxide and becomes quite exchangeable with hydroxyl ions.	Jones (1957)
Evidence indicates that soil reaction is the major controlling factor in the availability of molybdenum to plants. As the pH drops below 7, molybdenum appears to become less available and as the pH rises above 7, molybdenum becomes more soluble and thus more available.	Evans et al. (1951)
On reduction of soil acidity from pH 5 to pH 7, molybdenum uptake by plants is significantly increased. Uptake of molybdenum by plants in amounts toxic to animals normally takes place on alkaline soils or soils with high organic matter contents. Uptake of molybdenum from acid soils of a pH of 5 can also occur if the soil organic matter content is high.	Mitchell (1964)
On most soils tested, ammonium sulfate appears to decrease molybdenum contents of herbage from potentially toxic to animals to marginal or normal concentrations.	Williams & Thornton (1972)
In considering molybdenum in general and its movement in soils, a very high proportion of the element appears to be leached throughout soil profiles.	Jones & Belling (1967)
Molybdenum appears to be readily absorbed by soil. The first absorption within the soil may be through covalent bonding of soil surface hydroxyls or an exchange at surface hydroxyls.	Ellis & Knezek (1972)

Concentration	Reference
Under normal soil conditions up to approximately 90% of the molybdenum in the soil may occur in a form unavailable to plants.	Bould (1963)
Nickel:	
Nickel appears to be absorbed in the ionic form from the soil or culture solution. Nickel appears to be more easily absorbed by plants when applied in the ionic form. It has been observed to be taken up by plants at a rate of approximately ten times that of complexed nickel.	Crooke (1954)
No positive relationship exists between the nickel content of soil and that of plants unless the pH of the soil is considered. Soil values below pH 5.6 favor absorption of nickel while values of above 5.6 do not. Application of lime to acid soils appear to reduce the absorption of nickel by plants by raising the soil pH.	Vergnano (1953)
Nickel has been found as a soil contaminant in the area of smelting operations. Highest concentrations occur in the immediate area of the smelter and decrease quite rapidly with distance. The nickel appeared to be concentrated in the soil surface layer without movement through the soil profile.	Hutchinson & Whitby (1974)
In general, nickel in soil appears to have increased mobilization in profiles of poorly drained soils.	Swaine & Mitchell (1960)
Selenium:	
It appears that even in soil of low selenium content, drainage waters become enriched with selenium and that selenium is mobilized in the soil by irrigation.	Williams & Byers (1935)
Studies of toxic and non-toxic seleniferous soils has shown climate and the soil development process to be major factors in the availability to plants of the selenium in soils. The toxic soils in the U.S. are pedocal soils, which are alkaline in reaction, contain free calcium carbonate, and lie in regions of low rainfall, usually less than 20 inches mean annual precipitation. No acid soils are known to produce toxic vegetation. In acid soils, the selenium is probably in the form of insoluble ferric selenite. Selenium occurring in soils as selenate appears to be normally leached out. A partial measure of selenium's availability to plants is its solubility in water.	Lakin (1961)
It has been concluded that drastic leaching of soil with the addition of sulfur or gypsum appears to offer an effective method of reducing the danger of selenium in food crops grown on soils previously treated with sodium selenate.	Fuller (1946)

Concentration	Reference
In considering the water soluble selenium values of soil profiles from South Dakota, it appears that selenium concentrations increase with depth of the sample.	Moxon (1958)
A comparison of the selenium content of crops with amounts of water soluble selenium and organic selenium in soils show a relatively close relationship whereas a comparison of selenium content of crops with total selenium or acid soluble selenium shows practically no direct correlation.	Olson & Moxon (1939)
Under alkaline well-aerated soil conditions, the selenium in soil appears to become oxidized to selenates. Selenates are not strongly absorbed or fixed in alkaline soils and are generally quite available to plants.	Allaway (1968)
Zinc:	
Toxicity in plants has been observed with soil concentrations of approximately: 400 ppm	Barnette (1936)
It has been observed that less zinc is taken up by plants after lime has been applied to acid soil. This effect as the soil pH increases is generally attributed to the formation of insoluble zinc hydroxide. It is commonly thought that zinc availability in soil is at a minimum when the pH ranges from 5.5 - 7.0.	Seatz & Jurinak (1957)
Laboratory studies with soil columns showed practically no downward movement of zinc as a result of leaching. Tests show an appreciable amount of soil applied zinc may remain in the extractable form for several years. It appears that soil applied zinc is immobilized in the soil surface and remains where it is placed.	Brown et al. (1961)
The downward movement of zinc applied to the soil surface appears to be dependant on the type of soil. Zinc moved through the soil profile of sandy soils quite readily but in most other types of soils, little or no mobility was observed.	Barrows et al. (1960)
Long continued accumulation and decay of organic matter under trees and other heavy vegetation causes accumulations of considerable amounts of zinc which becomes easily fixed in the soil surface.	Hibbard (1940)
Zinc appears to exhibit very little mobility within soil profiles and remains relatively fixed in the soil surfaces.	Hodgson (1963)
The solubility of oxides and other naturally occurring compounds of zinc is extremely low and the absorption and binding of the element by soil colloidal particles is sufficiently strong to make it an important process in controlling the availability of zinc to plants.	Ellis & Knezek (1972)

Concentration

Reference

Zinc deficiencies in crops is not common on acid soils. In soils, zinc content is often higher in the topsoil and this quite possibly could be caused by plant residue deposition or by industrial emissions into the atmosphere with subsequent deposition on the soil surface.

Lucas & Knezek (1972)

Zinc deficiency is most likely to be found in plants growing on soils with calcareous surface horizons or on leach, acid, sandy soils. Zinc deficiency may also occur where the soil is high in phosphorus, due to interactions involving zinc, phosphorus and iron leading to poor utilization of zinc by plants.

Kubota & Allaway (1972)

Fluoride:

There seems to be no evidence that fluorides from the air build up in soils in sufficient quantities to adversely affect crops. Experimental plants without increased fluoride concentrations have been grown in soil from areas exposed for several years to airborne fluorides.

McClure (1969)

In order for soil fluoride concentrations to be reflected in increased fluoride levels of vegetation, a considerable portion of the total fluoride must be in soluble forms. Fluorides deposited on soil from various sources is converted to insoluble calcium fluoride and thus does not show noticeable effects on the fluoride concentrations of vegetation.

Jewell (1969)

Soluble fluorides in soil become toxic to vegetation at concentrations of approximately: 50 ppm

Bear (1957)

Injury to plants from soil fluorides taken up by the roots is very rare. However, under certain conditions, plants growing on acid soils will accumulate fluorides and exhibit injury symptoms identical to those caused by hydrogen fluoride fumes.

Allaway (1968)

Substantial amounts of the total soil fluorides are in insoluble forms and are not taken up by vegetation.

The amount of fluorine accumulated from the soil by plants is usually not closely related to the fluoride content of the soil. Soil type, calcium and phosphorus, and soil pH appear to be the pre-dominant controlling factors other than plant species. Toxic range for root plants of soluble fluoride is:

Brewer (1966)

100 - 200 ppm

Concentration

Reference

Fluorine added to the soil in the form of superphosphates appears to be retained by heavier textured soils. Sandy soils retain less added fluorides. The added fluorides do not appear to increase the fluoride contents of plants to a significant degree.

Robinson & Edington (1946)

Sulfur:

Soils have been shown to absorb sulfur dioxide directly from the atmosphere. The rate of absorption is dependent upon moisture in the air streams or soils. Sorption increases markedly in the presence of moisture.

Yee et al. (1975)

Direct soil absorption of sulfates decreases as the pH of the soil increases. The amount of sulfate absorbed is directly related to the concentration of sulfates in the exposure media, and increasing soil phosphate concentrations appear to reduce the amount of sulfate absorbed by soil.

Kamprath et al. (1956)

It has been observed that as the pH of the soil is changed from acid to neutral, there is a marked decrease in the amount of sulfate absorbed.

Mattson (1927)

In field studies, when large amounts of phosphate has been added to soil, very little sulfate is found in surface layers indicating that phosphate can replace most surface soil sulfate.

Ensminger (1954)

In studies involving sulfur dioxide and a smelting process, it has been observed that sulfur dioxide fumigation of soil near the smelter appeared to lower the pH of the surface soil layer (acidify) with the soil pH approaching normal with increasing distance from the smelter.

Whitby (1939)

The Effects of Selected Trace Elements
on Vegetation

Arsenic:	Concentration	Reference
Arsenic accumulation in plant root systems. Not essential for plant growth. Toxic to plants in seedling stage. Symptoms of toxicity: wilting leaves, retardation root and top development.		Liebig (1966)
Severely limits early growth stages of plants.		Williams and Whetstone (1940)
Toxicity of arsenic to plants depends on its solubility in water.		Shacklette et al. (1974)
Toxicity of water soluble arsenic to alfalfa and barley occurs at:	2.0 ppm	Vandecaveye et al. (1936)
Toxicity of arsenic to vegetation is a function of solubility and complex.		Woolson et al. (1971)
Symptoms of As toxicity to plants: slow stunted growth, late maturity, yellowing of leaves, appearance of moisture deficiency. Injury to alfalfa has occurred at:	2.0 ppm	Bear (1957)
Arsenic in soils causes retardation of plant growth at:	4.0 - 12.0 ppm	Federal Energy Admin. (1975)
Toxicity of As compounds to plants:		
Arsenites	10.0 ppm	
Arsenates	5.0 ppm	
Beryllium:		
Beryllium, as it presently occurs, does not represent a factor in the health of crops.		Tepper (1972)
Beryllium has been shown to exert a toxic effect on vegetation which exhibit a magnesium deficiency. The effects appear to come not so much from the beryllium concentrations, but from the deficient concentration of magnesium.		Hoagland (1952)
Cadmium:		
Cd appears to be absorbed by above ground plant parts. Many plants in high Cd polluted areas tend to build surface deposits of the element. Cd content of plants appears to increase with increasing soil concentrations.		Goodman & Roberts (1971)
There are no reports of Cd toxicity occurring naturally under field conditions in plants. Toxicity occurs primarily from industrial contamination.		Fleischer et al. (1974)
Vegetation grown on contaminated soil will accumulate soluble Cd which may cause a potential Cd toxicity hazard to humans.		Page et al. (1972)
Airborne Cd appears to accumulate in plants through a non-metabolic binding of the element on tissue cell walls.		Cutler and Rains (1974)
Concentrations of Cd that are toxic to plants are largely unknown. High levels of Zn usually accompany high levels of Cd in the environment and both may exert a toxic effect.		Shacklette (1972)

	Concentration	Reference
Cd when added in concentrations in excess of that normally found in plants has been seen to stimulate stomatal closure. The photosynthetic process has also been inhibited.		Bazzaz (1974)
Cd toxicity has been seen to occur in soybeans at: The primary visual toxicity symptom for wheat plants appears to be stunted growth. Cd excess may produce or aggravate iron deficiency in plants since symptoms resemble iron chlorosis. Aerial contamination of plants by cadmium appears to present the greatest danger to man and animals in terms of potential toxicity.	2.5 ppm	Hanhiri (1973)
Chromium:		
A concentration of chromium as the chromic ion or chromate ion at: produced iron chlorosis in sugar beets in sand cultures. The chromate ion appears to be more toxic than the chromic ion to vegetation.	8 - 16 ppm	Hewitt (1953)
Iron chlorosis in oat plants has developed at chromium concentrations of: Specific symptoms of chromium toxicity in oats begins to appear at: Toxicity symptoms in oat plants are stunted growth with narrow brownish-red leaves and poorly developed roots. The principal accumulation and toxic effect of chromium appears to occur in the root system.	5 - 10 ppm 15 - 50 ppm	Hunter & Vergnano (1953)
Toxicity to tobacco plants has occurred at chromium levels of: Toxicity symptoms in corn plants has occurred at chromium levels of: Toxicity symptoms observed in corn: Plants become severely stunted, with the leaves showing a tendency to roll and turn greenish-purple in color.	5 ppm 10 ppm	Soane & Saunder (1959)
Chromium has not been noted to have caused damage to plants of importance in agriculture under field conditions.		Smith (1972)
Detrimental effect of vegetation from chromium may occur at concentrations of: Chromium is not considered as essential to plants on the basis of present evidence, even though some growth stimulatory effects have been observed. When naturally occurring chromium toxicity to plants has been suspected, it is not certain that chromium is the only potentially toxic element involved.	10 - 100 ppm	Allaway (1968)
The concentration of chromium in oat plants which appears to cause marginal toxicity to the plants is:	124 ppm	Anderson et al. (1975)

Copper:	Concentration	Reference
Symptoms of copper toxicity appear in citrus seedlings in concentrations of:		Lagerwerff (1967)
Clover and alfalfa are particularly sensitive to excessive copper, showing stunted growth, and dieback.	<50 ppm	
Copper toxicity in vegetation has been observed at concentrations of:	20 ppm	Allaway (1968)
In a wide variety of plants, Cu deficiency is characterized by levels of less than:	4 ppm	
Range of copper concentrations required for normal growth:	5 - 20 ppm	
The availability of copper to plants is dependent upon soil pH, but does not normally increase until pH falls below five. High levels of nitrogen and phosphorus can encourage deficiency of Cu in vegetation. Excessive amounts of zinc can actuate Cu deficiency also.		Lucas & Knezek (1972)
Severe copper deficiencies have been induced in citrus by applying phosphorus at a concentration of:	180 ppm	Olsen (1972)
Toxic effects of copper have been decreased by additions of iron but effects have not totally been overcome with iron applications. The application of excessive zinc has been shown to induce copper deficiency in wheat and barley.		
Various species of plants show different symptoms of Cu toxicity, but in general early stages show reduced growth, reduced yield. Moderate to acute toxic stages show terminal growth with dieback of growing points a common symptom. Other symptoms such as chlorosis and necrotic spotting may occur. Many plants show thickening and abnormally dark coloration of rootlets.		Reuther & Labanauskas (1966)
Symptoms of copper deficiency in oat plants have appeared under field conditions at levels of:	2.0 ppm	Teakle et al. (1941)
Copper deficiency in plants symptoms: reduced growth, color change to gray-green or blue-green, dieback of leaves. Wheat, barley and oats are very sensitive to copper deficiency.		Nelson et al. (1956)
Copper deficiency may be indicated in alfalfa at concentrations of:	<1 - 2 ppm	Dye (1962)
No natural occurring toxicity to alfalfa has been recognized.		
In cereals and grasses, Cu concentration increases linearly with increasing nitrogen contents, with a tendency toward higher Cu-N ratios as concentrations of both elements increase. The effects of copper contamination to soil with relation to vegetation are extremely dependent on soil type and pH.		Gladstone et al. (1975)
Copper and nickel exhibit a relationship in instances of Ni toxicity to vegetation. Increasing		Mizreno (1968)

	Concentration	Reference
the Cu-Zn ratio in plants has reduced the degree of nickel toxicity symptoms in plants.		
Copper concentrations in the upper portions of plants tends to decrease with increasing maturity.		Fleming (1965)
Zinc deficiency in plants appears to be aggravated by increasing copper concentrations in plant roots and tops.		Chaudhry & Lonerogan (1970)
Copper toxicity was induced in plants at a level of: Specific symptoms begin to appear between:	20 ppm 10 - 20 ppm	Hunter & Vergnano (1953)
Lead:		
Lead content of rye grass appears to increase with increasing rates of lead addition to the soil. Lead appears to be primarily associated with the root structure and it is concluded that roots of actively growing rye grass provide a barrier which restricts the movement of excessive amounts of lead to above-ground plant parts.		Jones et al. (1973)
Roots appear to accumulate a surface lead precipitate from the soil and slowly accumulate lead crystals in cell walls. This lead is taken up and distributed throughout the above-ground plant parts.		Malone et al. (1974)
Excessive concentrations of lead, when applied to soil, show the effect of decreasing net photosynthesis and transpiration to both soybeans and corn. Corn tends to be a lead accumulator plant. Airborne lead appears to cause a possible interference with gas exchange in the plants.		Bazzaz (1974)
Lead content of the tops of plants appears to correlate poorly with the soil lead concentrations. Root concentrations appear to correlate quite well. Under conditions of adequate sulfur supply, rye grass appears to restrict the movement of lead to upper plant parts. Under conditions of sulfur deficiency, lead in plant tops appears to increase significantly.		Jones et al. (1973)
The effects of lead on plant growth appear to be accentuated under conditions of phosphate deficiency.		Koeppel & Miller (1970)
Various vegetables and cereal crops do not appear to be significantly affected by the concentration of lead in the air. The inedible portions of the plants do appear to absorb lead from the air but the soil appears to be the primary source of lead in edible plant portions.		Ter Haar (1970)
Lead originating from contamination or from decayed plant tissue tends to be retained in the soil surface. Surface rooting plants appear to be		Lagerwerff (1967)

Concentration	Reference
more significantly affected by soil lead deposition than deep rooting plants. The liming of soil appears to diminish the toxicity of high concentrations of soil lead to plants.	
Lead uptake and resulting toxicity to plants appears to be related through the action of calcium. The concentration of calcium appears to show depressing effect on the lead uptake of the plant.	Wallace (1971)
Lead does not appear to accumulate in young, rapidly growing oat plants until they reach the early stages of maturity. The more advanced the stage of maturity, the higher the lead levels became in the vegetation studied.	Rains (1971)
Mercury:	
Mercury has a strong affinity for sulfur, particularly for sulphydral groups and proteins. Bound to proteins in a cell membrane, mercury may alter the distribution of ions electric charge potentials and thus interfere with the movement of fluids across the membranes.	Goldwater (1971)
It has been found that plants such as carrots, potatoes, turnips, lettuce, and beans grown in soil treated with organic mercury compounds accumulate very little in the edible parts of the plants.	Wallace et al. (1971)
Mercury enters in several ways, first by absorption from the soil or mercury in foliar sprays, dust, rain, or in vapors exhaled by the soil under day-night temperature gradients may enter the leaf tissue. Plants both inhale and exhale gaseous mercury through the stomata.	Lagerwerff (1972)
Molybdenum:	
Average molybdenum content which appears to produce toxicity for animals in many forage plants ranges:	Cunningham et al. (1953)
10 - 26 ppm	
Molybdenum toxicity for livestock from plants is usually observed when concentrations exceed:	Hewitt (1963)
10 ppm	
Legumes are able to absorb amounts of molybdenum harmful to cattle from soils that contain as little as 1.5 - 5.0 ppm total molybdenum.	Barshad (1948)
Molybdenum has been found to be an essential element for most plants. The tissue concentration requirement appears to be in a range of:	Gupta (1969)
0.5 - 5 ppm	
Pasture plants considered toxic to cattle and sheep usually contain in excess of:	
10 ppm	
Most plants appear to tolerate relatively low levels of tissue-bound molybdenum. No toxicity was observed in alfalfa at tissue concentrations of:	
372 ppm	

	Concentration	Reference
Molybdenum is required in all plants for protein synthesis and symbiotic nitrogen fixation in legumes. Molybdenum is essential in the enzyme reductase which reduces nitrate to nitrite in the process of protein synthesis.		Boswell & Anderson (1969)
Optimum tissue levels of molybdenum for plants grown in sandy, clay-loam soils appears to be as follows:		Gupta (1970)
alfalfa:	0.12 - 0.46 ppm	
red clover:	0.46 - 1.08 ppm	
timothy:	0.14 - 0.17 ppm	
brussel sprouts:	0.11 - 0.22 ppm	
spinach:	0.15 - 0.24 ppm	
Injury from molybdenum appears in tomato plants at concentrations which exceed:	10 ppm	Arnon & Stout (1939)
Molybdenum when applied to soil at the concentration of 5 ppm has caused orange discoloration in flax with stunted root and plant growth. It was concluded that molybdenum is intimately associated with the regulation of the effects of manganese, zinc, copper, nickel, and cobalt on the physiological availability of iron to the plant.		Millikan (1947)
It appears that for most vegetation the essential level of tissue molybdenum is:	0.02 ppm	Piper (1940)
Molybdenum serves in plants as a catalyst in enzyme systems that function in reducing nitrate to ammonium in preparation for the synthesis of amino acids in proteins. As far as is now known, toxicity of molybdenum enters the agricultural picture only in relation to livestock.		Bear (1957)
No injury to most plants is seen even where the molybdenum concentration exceeds:	100 ppm	Allaway (1968)
The uptake of molybdenum by plants is reduced by sulfur since sulfur and molybdenum are two divalent ions of approximately the same size. Sulfur thus appears to inhibit molybdenum utilization within the plant. The effect appears to take place at the sight of uptake on the plant roots. Copper also appears to interfere with the role of molybdenum in the enzymatic reduction of nitrates causing molybdenum deficiency symptoms in plants.		Olsen (1972)
Molybdenum toxicity symptoms in alfalfa, if such can exist, are unknown at present.		Dye (1962)
Oat plants appear essentially normal with concentrations of: Slight chlorosis was observed in oats with the leaf tips showing a purplish color at molybdenum concentrations of:	50 ppm	Hunter & Vergnano (1953)
	100 ppm	

	Concentration	Reference
The size of the root structure of oat plants appears to be reduced at levels of: Only concentrations of molybdenum at 200 ppm appear to alter the major nutrient status of oat plants.	200 ppm	
Nickel:		
Nickel absorption by plants has been observed to damage the roots. In tomatoes, nickel absorption damaged the root system causing a reduction in the absorption and translocation of all other nutrient elements in the study.		Knight & Crooke (1956)
Nickel appears to be translocated in the conducting system of plants and moves to the areas of greatest metabolic activity where it becomes concentrated.		Vergnano & Hunter (1953)
Nickel sulfate solutions have shown a marked stimulatory effect on the germination of pea, bean, wheat and castor seeds when applied at concentrations of: The germination of these seeds was adversely affected at levels of:	26.3 ppm <26,000 ppm	Choudhuri & Bhatnagar (1952)
Seed treatments with nickel appear to produce maximum growth of wheat shoots and roots at concentrations of: Growth appears to be inhibited at levels of:	100 ppm 250 ppm	Tsui (1955)
Nickel appeared to be highly toxic to buckwheat seedlings when applied at a concentration of:	5.87 ppm	Cotton (1930)
Nickel appears to suppress the growth of soybeans. Growth suppression appears to be due to deficiencies of both phosphorus and iron which were caused by the addition of excessive nickel. Nickel treatments appeared to reduce the total iron content of various plants.		Roth et al. (1971)
Nickel causing toxicity in oat plants did not markedly reduce the total iron content of plants. It appeared that nickel toxicity may cause a localized iron deficiency within plants rather than a total reduction of iron concentration.		Crooke & Knight (1955)
There appears to be a reciprocal relationship between iron and nickel content of leaves. Nickel is reduced by high concentrations of iron in solution and the iron content is reduced by high concentrations of nickel.		Crooke et al. (1954)
The severity of nickel toxicity to oat plants appears to increase with increasing manganese concentrations. The action of the two metals appear to increase the absorption of iron by the plant but decrease its metabolism.		Williams (1967)

Concentration	Reference
One of the main toxic symptoms produced by nickel is the chlorosis or yellowing of leaves usually followed by necrosis. Other symptoms include stunted growth of the root and shoot, deformation of various plant parts, unusual spottings, and in extreme cases, death of the plant. Nickel appears to regulate mineral metabolism and enzyme activity in plants. At non-phytotoxic levels, it has been shown to increase yield of some crops. Nickel has not been ranked as an essential in plant nutrition.	Mishra & Kar (1974)
From the literature, it appears that marginal toxicity in oat plants will occur at tissue levels of approximately:	Anderson et al. (1973)
50 - 150 ppm	
Selenium:	
Selenium in nutrient solution has been toxic to wheat plants in the absence of sulfur at concentrations of:	Hurd-Karrer (1934)
0.1 ppm	
Toxicity appears to be eliminated with the addition of sulfur. It has been shown that sulfur concentrations of 192 ppm prevent plant injury by selenium at concentrations of:	
16 ppm	
Selenium has shown stimulation of growth in wheat plants when applied to concentrations of:	Perkins & King (1938)
0.4 ppm	
1.0 ppm	
2.6 ppm	
Toxicity in wheat occurred at:	
6.4 ppm	
It appears that various plants which have high sulfur requirements also store relatively large quantities of selenium. Some of these crops are broccoli, cabbage, cauliflower, mustard and onions.	Hurd-Karrer (1937)
Visual symptoms of excess selenium have never been observed in field plants growing on naturally seleniferous soils. Most all visual toxicity symptoms have been produced in greenhouse experiments by the addition of selenite, selenate, or organic selenium to the root medium. Toxicity symptoms in cereal grains usually appears as a snow white iron chlorosis of the leaves. Stunting of growth is indicative of less severe injury.	Gange (1966)
In wheat, a pinkish coloration of selenite-injured roots accompanies the chlorosis symptoms.	
The literature contains very little information concerning data of what threshold values of selenium exist for various plants.	
Comparative toxicity of selenates and selenites to plants depend on the concentration of available sulfate. Toxicity of all selenates decreased progressively with the increasing sulfate sulfur while that of selenites was greater with higher concentrations of sulfate.	Hurd-Karrer (1937)

Concentration	Reference
<p>Toxicity of selenium to wheat and buckwheat appears to be proportional to the concentration added as sodium selenite to soil cultures and solution cultures. Decreased growth rate occurred with application of:</p> <p>Extreme chlorosis and premature plant death occurs at:</p> <p>Selenite was observed to be more poisonous to animals than plants. Buckwheat plants that exhibited no symptoms of injury except for slight dwarfing, contained enough selenium to produce death in rats in nine weeks of dietary intake.</p>	<p>Martin (1936)</p>
<p>1, 2, & 4 ppm</p> <p>8, 16, 32, & 64 ppm</p>	
<p>Plants have been put into three groups by Miller and Byers according to the ability to assimilate selenium.</p> <p>Group 1: plants with limited tolerance, up to 3 ppm.</p> <p>Group 2: plants with a moderate tolerance, up to 30 ppm.</p> <p>Group 3: plants with very high tolerance to selenium.</p> <p>Most grasses, clovers, and garden vegetables are included in Group 1. Most all cereal grains are in Group 2.</p>	<p>Fleming (1965)</p>
<p>Vanadium:</p> <p>Vanadium oxide as ammonium metavanadate showed the following effects on rice seedlings:</p> <p>increased growth: 150 ppm</p> <p>toxicity symptoms: 500 ppm</p> <p>plant death: 1000 ppm</p> <p>There appears to be no reports in the literature indicating either deficiency or toxicity of vanadium in vegetation under field conditions. Vanadium appears to have some function in the growth of nitrogen fixation processes of certain soil microorganisms but its essentiality for crop plants has not been conclusively demonstrated.</p> <p>In studies using excised barley roots, it was noted that the rate of uptake of vanadium by the plant was highest at an acid pH but dropped to very low levels at alkaline pH levels. It does not appear that vanadium is actively absorbed by plant roots.</p> <p>Vanadium in nutrient solutions is commonly harmful to plants at concentrations of:</p> <p>Vanadium content of above-ground parts of plants rooted in highly calcareous soils is very high. The absorption and translocation of vanadium by several plant species was found to parallel that of selenium.</p>	<p>Chiu (1953)</p> <p>Pratt (1966)</p> <p>Welch (1973)</p> <p>Cannon (1963)</p>
<p>10 - 20 ppm</p>	

	Concentration	Reference
Plant species that absorb large amounts of calcium are most tolerant of high vanadium soils, due to vanadium being precipitated in the roots.		
Zinc:		
It appears that the uptake of zinc by barley is counteracted by phosphorus applications at various stages of growth. It is suggested that in areas where regular phosphorus applications to soil are necessary, a zinc deficiency in vegetation may result.		Montsara (1973)
From the literature, it appears that in a variety of plants, deficiency levels are characterized by zinc concentrations of less than:		Chapman (1966)
Ample levels commonly fall in a range of:	20 - 25 ppm	
Excessive zinc concentrations in plants generally exceed:	25 - 150 ppm	
	400 ppm	
Alfalfa has shown symptoms of zinc deficiency at tissue concentrations of:		Millikan (1953)
	8 - 13 ppm	
In zinc toxicity studies with oat plants, it was observed that toxicity symptoms appear in mature leaves at zinc concentrations of:		Hunter & Vergnano (1953)
	1700 - 7500 ppm	
In studies with young oat plants, it was observed that deficiency symptoms would appear at tissue zinc concentrations of less than:		Wood & Sibly (1950)
	20 ppm	
Tomatoes grown in a solution medium have shown symptoms of zinc toxicity in leaves at concentrations of:		Lyon et.al. (1943)
	526 - 1489 ppm	
It is postulated that zinc is necessary for chlorophyll formation and growth of plants.		Camp (1945)
Corn plants show moderate symptoms of deficiency at zinc tissue concentrations of:		Hiatt & Massey (1958)
Normal appearing corn plants were found to contain:	9 ppm	
	16 ppm	
In laboratory studies, it was shown that different varieties of soybeans exhibit a striking variation in reaction of zinc concentrations in slightly acid or neutral nutrient solutions. The degree of plant damage from zinc appears to increase with the decreasing pH of the solution. That is, the more acid the solution, the greater the degree of plant damage caused by zinc.		Earley (1943)
Zinc toxicity problems in plants has been overcome by liming the soil.		Bear (1957)
Zinc in nutrient solutions has been shown to greatly increase plant growth and dry matter yield at concentrations of:		Jelenkovic (1969)
	0.5 mg/liter	

Concentration	Reference
Zinc was applied to soil at the rate of 11 kg/ha for six successive years without producing toxic effects in soybeans. The high tolerance was partly attributable to a decrease uptake in zinc at near neutral levels of pH of the soils. It was indicated that very high concentrations of zinc do not increase the concentrations in soybean seeds to levels that would preclude their use as animal feed.	Martens et al. (1974)
In plants, it appears that root absorption of zinc is greater than the zinc translocated to the tops of plants. It also appears that the uptake of iron is depressed with the application of high concentrations of zinc salt or combined zinc and iron salts.	Lopez & Graham (1973)
It is postulated that alkaline earth cation effects are important in the zinc nutrition of plants in soil and solution cultures in that the addition of such substances may result in zinc deficiency in plants where none previously existed.	Chaudry & Loneragan (1972)
In field experiments, seedlings growing in soil ranging in zinc concentrations from 100-300 ppm showed no signs of toxicity, even with the foliar levels reaching to:	Bauchauer (1973)
2120 ppm	
In experiments with grasses and clovers, it appears that zinc content in plants varies with species and stage of maturity. Zinc contents of grasses decreased with increasing maturity.	Fleming (1965)
Experiments show that copper appears to strongly inhibit the absorption of zinc by barley roots. It appears to be possible that copper and zinc compete for the same absorption sites on plant roots.	Schmid et al. (1965)
Fluoride:	
Fluorides originating in the soil tend to accumulate in the roots of plants. High concentrations of root-acquired fluoride causes necrosis of the internal areas of leaves of some plant species. Airborne, leaf-acquired fluoride causes marginal and tip necrosis of leaves.	McClure (1969)
Leaves remove gaseous fluoride from the air with accompanying accumulation in the tissue. Acute fluoride injury symptoms: Occurrence of necrotic tissue along margins and tips of leaves along with possible streaking or spotting. The effects vary with the species of plant. In chronic fluoride injury, a loss of chlorophyll occurs resulting in a chlorotic or mottled pattern.	

	Concentration	Reference
Plants low in calcium appear to be more severely damaged by fluoride.		
Soil pH appears to play a role in the toxicity of fluoride to vegetation. An acidic pH in soil requires small concentrations of fluoride to produce injury. All vegetation studied in soil pH ranges of 4.5 to 6.5 were injured by fluoride concentrations of:	360 ppm	Prince et al. (1949)
Concentrations of fluorides causing toxicity vary with type of soil, pH, and plant species.		
Evidence that fluorine performs a vital function in the nutrition of plants has not been produced. Heritage plants are usually low in fluorine which tends to reflect the limited capacity of most plant species to absorb fluorine from the soil.		Underwood (1962)
The presence of abnormally high fluoride concentrations in plant tops with low concentrations in the roots indicates that atmospheric fluoride is the principle source of the element to vegetation. A reverse order concentration indicates the soil as the source of fluorides in investigative studies.		Brennan et al. (1950)
Many species of plants have shown symptoms of chronic fluoride toxicity after extended periods of exposure to hydrogen fluoride in the air at concentrations of:	5 - 7 ppb	Brewer (1966)
Intervascular chlorosis appears to be a primary symptom of chronic fluoride toxicity.		
Corn leaves when exposed to:	5.0 ppb	Adams et al. (1957)
of hydrogen fluoride have shown toxicity symptoms with actual leaf concentrations of approximately:	180 ppm	
The primary danger of fluoride injury to plants appears to depend upon the absorption of fluoride into the tissue. Fluoride gases are more readily absorbed than solid fluoride compounds deposited on leaf surfaces. Injury develops under widely fluctuating concentrations or brief exposure to high concentrations.		Pack & Adams (1966)
Fluoride containing gases are much more toxic to vegetation than equivalent atmospheric concentrations of other phototoxic gases.		Adams (1956)
Fluoride has been observed to accumulate in vegetation at atmospheric concentrations of:	0.1 - 0.7 ppb	
Data indicates that fluorine is a cumulative systemic poison in vegetation.		

Sulfur:	Concentration	Reference
Visual symptoms of bean and tomato seedling leaf injury have been observed after 48 hours of fumigation with sulfur dioxide at a concentration of:	0.5 ppm	Solberg & Adams (1956)
Sulfur dioxide causes two types of injury to the leaves of plants. Acute injury shows marginal or interveinal collapsed areas while chronic injury shows areas of leaf cell damage but not total collapse.		Thomas, M. D. (1958)
Various amounts of leaf destruction on alfalfa have been predicted experimentally at the following levels at 1-hour exposure:		Thomas & Hill (1935)
slight injury	0.94 ppm	
50% leaf destruction	2.1 ppm	
total leaf destruction	3.2 ppm	
One-hour exposure to sulfur dioxide may cause injury to the following plants at the indicated concentration levels:		O'Gara & Hendricks (1956)
Alfalfa:	1.2 ppm	
Barley:	1.2 ppm	
Wheat:	1.8 ppm	
Plant injury is any measurable response of a plant to air pollution. Damage is any identifiable and measurable adverse effect upon the desired or intended use of the plant.		Heggestad & Heck (1971)
Detectable injury to sulfur dioxide sensitive plants will occur under average conditions with a 4-hour exposure time and sulfur dioxide concentrations of:	0.5 ppm	Thomas (1961)
Acute injury to trees and shrubs has occurred after 7-hour exposure time of sulfur dioxide at a concentration of:	0.5 ppm	Scheffer & Hedgcock (1955)
Alfalfa and barley are among the most sensitive to ambient sulfur dioxide. Incipient damage markings on alfalfa under conditions of maximum sensitivity occur after one hour at a concentration of:	1.25 ppm	Middlcton et al. (1958)
In experiments with sulfur dioxide and ozone, it has been observed that sub-injury threshold levels of each gas when mixed, caused plant damage greater than the additive effects alone. This suggests that this combination of pollutants lowers the threshold for plant injury and effects are synergistic.		Menser & Heggestad (1966)
Barley leaves exposed for 72 hours with sulfur dioxide showed symptoms of leaf necrosis at a concentration of:	0.3 ppm	Mandl et al. (1975)
The addition of H_2O_2 at .0009 ppm to the sulfur dioxide showed no additional leaf injury.		
The degree of plant injury by		Whitby (1939)

Concentration	Reference
sulfur dioxide at any given concentration level and period of exposure is highly dependent upon factors favoring stomata opening and photosynthesis such as relative humidity and light intensity at time of exposure.	
The degree of damage to vegetation by sulfur dioxide is associated with high humidity (>70%), moderate temperature (>40°F), high light intensity, adequate moisture supply, and wind stability for exposure periods of three hours or more, in addition to the ambient concentration of sulfur dioxide.	Holmes et al. (1915)
Leaf destruction in vegetation is more directly dependent upon the amount of gas actually absorbed than on the concentration of sulfur dioxide gas in the air. Exposures which result in severe injury to given plants under any set of conditions are innocuous under others.	Middleton et al. (1958)
Exposures of sulfur dioxide after long duration on vegetation may cause toxicity to sensitive plants at concentrations of: Concentrations demonstrated to be in the range of non-influence have been reported as:	Katz (1949)
	>0.4 ppm
	0.10 - 0.20 ppm
Common small grain and vegetable crops have shown no symptoms of injury after 4-hour fumigation of sulfur dioxide at levels up to: Plant injury has been observed when sulfur dioxide was mixed with nitrogen dioxide at levels of:	Tingey et al. (1971)
	50 ppm
	5 - 25 ppm
Different plants vary widely in their susceptibility to injury by sulfur dioxide. Alfalfa and barley are the most sensitive.	Thomas et al. (1950)

The Effects of Selected Trace Elements
on Animal Nutrition and Health

Arsenic:	Concentration	Reference
Arsenic is not considered essential for animal growth and reproduction. As retention and excretion depends on the arsenic compound and species of animal.		Underwood (1962)
Small amounts of arsenic in animal diets may counteract selenium toxicity.		Allaway (1968)
Primary danger of arsenic toxicity to livestock and humans is from plants contaminated by dust containing arsenic compounds.		Underwood (1962)
Arsenic in the form of arsenic acid shows little retention in the tissues of cattle and is not excreted into the milk. There is no established effect of this compound.		Peoples (1964)
Beryllium:		
The present occurrence of beryllium does not represent a factor in the health of domestic or wild animals. Beryllium dissolved in water or food supplies is not known to be of health significance unless very high experimental concentrations are achieved.		Tepper (1972)
Beryllium has been shown experimentally to induce rickets in animals. The phenomena appears to be related to the uptake of calcium and phosphorus from the gastrointestinal tract and does not appear to be related to man. Tumors of the lung and bone have also been shown experimentally in animals with no apparent relationship to man.		Tepper (1972)
Cadmium:		
Chronic cadmium poisoning has occurred in a horse after long-term ingestion of hay and grasses containing:	7.6 - 9.9 ppm	Goodman & Roberts (1971)
(incident report)		
In a 12-week study, no toxic effect was seen in calves being fed a ration containing 40 ppm Cd, and 22.4 ppm zinc.		Powell et.al. (1964)
Cadmium content of all animal tissues was found to increase with increasing dietary cadmium intake. The high Cd intake was found to depress copper, iron, and manganese in various tissues. Zinc concentrations in animal liver and kidneys was seen to significantly increase at dietary Cd levels of:	15 ppm	Doyle & Pfander (1975)
The growth rate of young pigs is shown to decrease as a function of dietary cadmium level intake.		Cousins et.al. (1973)
Cessation of growth (in pigs):	1350 ppm	
Calcium levels in the animal tissues were not affected by high cadmium intake. Toxicity symptoms appear primarily where there are high levels of cadmium and deficient levels of calcium.		
Selenium has been shown to exhibit a protective effect against cadmium toxicity effects in animal experiments. Increasing the concentration of zinc tends to reduce the protective effect of selenium.		Mason and Young (1967)

Chromium:

Concentration

Reference

A review of the literature indicates that there have been no episodes comparable to those of selenium or arsenic, etc. in which farm animals have been poisoned by excess chromium intake due to environmental contamination.

Smith (1972)

Chromium has been classified as a low toxicity element meaning exposure required for detrimental effects to the animal from dietary intake must be:
Chromium in the hexavalent form is especially toxic to animals at high levels.

Allaway (1968)

>100 ppm

Copper:

Normal animal diet requirement of copper:

1 - 10 ppm

Allaway (1968)

However, this is dependent on accompanying levels of Mo in the diet. Dietary levels of Mo of 10 - 20 ppm, are nearly always associated with some evidence of disturbed copper metabolism in ruminant animals.

Chronic copper poisoning of calves, with death resulting in 20 and 21

Todd & Thompson (1965)

weeks has occurred at a dietary concentration of:
Symptoms: hemolytic crisis and induced jaundice.

500 ppm

Adult cattle will tolerate:
Calves will tolerate:
Calves can tolerate dietary levels of:

5 gm/day

1 gm/day

72 and 115 ppm

Phases of copper poisoning in animals (1) tissue accumulation (2) development of toxicity symptoms. Site of tissue accumulation is the liver. Toxicity signs may develop when liver concentration reaches:

Todd (1962)

4000 - 5000 ppm

Sheep are the most susceptible animal to copper toxicity with calves being next. Death in sheep has occurred in one to two months at levels of intake:

1 gm/day copper sulfate

Chronic toxicity in sheep can develop over long periods in concentrations of:

30 ppm

Death from chronic copper poisoning of sheep has occurred at:

35 ppm

In diets very low in molybdenum, toxic jaundice has occurred at:

15 - 20 ppm

Very young calves have shown toxicity symptoms at:

115 ppm

Death has occurred in pigs on feed concentrations of:

130 ppm

Excessive intake of molybdenum and sulfate limit copper storage in the liver and are used effectively in reducing the toxicity of copper.

Levels of copper in herbage as related to the needs of grazing animals.

Gladstone et al. (1975)

deficient
marginal
adequate

<3 ppm

3 - 5 ppm

>5 ppm

C3-141

Concentration	Reference
Cadmium appears to be antagonistic to copper. High Cd levels interfere in the protein synthesis necessary for copper absorption, which decreases copper contents of maternal and fetal tissues.	Hennig et al.
Toxic syndrome in livestock chronic copper poisoning: (1) period of passive accumulation in tissues; several weeks to a year, usually with no symptoms. (2) toxic phase: hemolytic crisis. Animal becomes dull, lack of appetite, excessive thirst, jaundice.	Todd (1969)
Excessive zinc and iron added to diets of copper-poisoned animals causes a reduction in accumulated copper and receding symptoms of copper toxicity.	Suttle and Mills (1966)
Molybdenum and copper are antagonistic in animal metabolism. Cu controls the pathological effects of Mo and Mo inhibits copper deposition in the liver.	Cunningham (1950)
One of the primary symptoms of high copper intake in pigs is iron deficiency. Copper appears to impair iron absorption from the gastrointestinal tract. Toxicity in hogs has appeared at:	Gipp et al. (1974)
250 ppm	
Lead:	
Toxicity of lead compounds to cattle and horses have been observed when concentrations in total ration dry matter have reached:	Hammond & Aronson (1964)
150 ppm	
No toxic effects have been observed in cattle after two years on a total lead intake of:	Allcroft (1950)
5 - 6 mg/kg dry wt.	
Toxicity has been observed in horses on pasture grasses which contain a dry weight concentration of:	Aronson (1971)
80 ppm	
All domestic species of livestock with lead poisoning exhibit varying degrees of derangement of the central nervous system. Chronic lead poisoning symptoms: Cattle: Blindness, grinding of the teeth, moving in a circle and ataxia. Sheep: Depression, anorexia, abdominal pain and usually diarrhea.	
Chronic lead poisoning symptoms in the horse: depression, stupor, knuckling at the fetlocks, laryngeal paralysis and anemia.	Clarke & Clarke (1967)
Apparent lethal dose of lead oxide to a mature cow appears to be:	White et al. (1943)
4.8 mg/kg body wt.	
Lead is one of the most common causes of poisoning in livestock in the U.S. The toxicity of lead varies with many factors and species of animals and within individual species.	Buck (1970)

	Concentration	Reference
Concentrations of lead acetate causing death in young cattle:	200-400 mg/kg body wt.	
Older cattle and sheep:	600-800 mg/kg body wt.	
Lead poisoning in cattle has developed in 6 - 8 weeks on total daily intake of:	6 - 7 mg/kg body wt.	
Lead is a cellular poison and the clinical signs are usually manifested by some form of central nervous system disorder.		
Death of young calves up to 4 months in age may result from daily lead acetate intake of:	0.2-0.4 gms/kg body wt.	Allcroft & Blaxter (1950)
Non-pregnant sheep and cattle can survive up to one year without toxicity symptoms on a total daily intake of:	5 mg/kg body wt.	
Death has resulted in cattle after 220 days on dietary intake levels of:	8 mg/kg body wt.	
Data indicates that pregnant sheep are more susceptible to lead and that abortion may follow continuous ingestion of lead in quantities which appear to be safe for non-pregnant sheep.		
Lead poisoning in animals and man has been seen to cause anemia, fatigue, weight loss, chronic renal disease, and neurological alterations manifestes as intestinal colic, neuropathy and encephalopathy. Antagonistic effects in biological systems have been observed for lead versus Mn and Mo, zinc, copper and iron and iodine.		Vallee & Ulmer (1972)
Lead poisoning in cattle and sheep has been observed on dietary intake of forage materials containing:	25 - 46 ppm	Dunn & Bloxan (1932)
Lead contamination of soils in the area of a smelter has been linked to lead toxicity in horses even though ambient air and drinking water concentrations of lead were within acceptable limits.		Schmitt et al. (1971)
Mercury:		
Methyl mercury accumulates in animal tissue because of long retention time in tissue. Most of the mercury found in animal tissue is methyl mercury.		Hammond (1971)
There is considerable risk for accumulation of methyl mercury in the tissues of mammals with prolonged exposure to methyl mercury compounds. The risk is due to very slow tissue elimination and a biological half-life which varies from 20 - 70 days in different species.		Berglund & Berlin (1969)
Depending on the species, central nervous system disorders with neurological symptoms seem to appear at mercury concentrations in the brain tissue of 8 mg/gram or more.		
Little is known about the dose level of mercury at which the first detectable toxicity signs or changes first appear.		

	Concentration	Reference
No qualitative or quantitative data has been found concerning mercury poisoning for animals exposed to typical environmental conditions.		Stahl (1969)
Dogs have shown no signs of mercury poisoning after forty days of exposure to an arial concentration of:		Frazer et al. (1934)
The dogs showed central nervous system effects after forty days of exposure to an arial concentration of:	3000 $\mu\text{g}/\text{m}^3$	
Death has been the result in dogs after exposure to mercury vapor at concentrations between:	6000 $\mu\text{g}/\text{m}^3$ 6000-20,000 $\mu\text{g}/\text{m}^3$	
Molybdenum:		
Toxicity and death in cattle has occurred of forage concentrations of:		Cunningham et al. (1953)
Typical symptoms include severe diarrhea, emaciation, anemia, fading of hair color, excessive craving for salt, all of which usually end in death. Evidence has been obtained to show that in the early stages of molybdenum intoxication, molybdenum may pass through into the milk of cattle and affect young calves.	25.0 ppm	
Dietary molybdenum in the absence of sufficient copper appears to create typical symptoms of molybdenum toxicity with accompanving loss of weight, scouring, and reduced feed consumption. Molybdenum appears to complex copper and that copper in the complex state is biologically inactive in the animal.		Clawson et.al. (1972)
Molybdenum is rapidly absorbed from the intestinal tract of animals. This applies particularly to water soluble forms.		Underwood (1962)
Molybdenum is excreted mainly in the urine of animals. Sulfates by some mechanism appear to reduce molybdenum retention in the tissues of cattle presumably through the increase of urinary excretion.		
Molybdenum in very small concentrations has been shown to produce a significant growth response in lambs. This response is believed to be due to the action of molybdenum in increasing cellulose degradation by rumen microorganisms.		
One of the features of severe molybdenosis known as teart in cattle remains obscure, this is primarily the mechanism of the protective action of copper. The tolerance of animals to molybdenum appears to be affected by the chemical form in which the element is administered, the copper status and intake of the animal, and the organic sulfate content of the diet.		

	Concentration	Reference
Horses and pigs appear to be among the most tolerant of high forage molybdenum concentrations. No ill effects were seen after three months of feed levels of: However, the effect of molybdenum depends on the copper and sulfate status of the diet.	1000 ppm	
It has been shown that chronic copper poisoning associated with extremely high liver copper levels in sheep appears under conditions of moderate copper intakes and very low intakes of molybdenum and sulfate.		
It is felt that molybdenum concentrations at levels greater than 2 ppm in forage may be of importance in molybdenum induced hypocuprosis in cattle.		Allaway (1973)
Specific symptoms of molybdenum intoxication in cattle were observed where the native vegetation contained molybdenum concentrations; No symptoms were observed with forage concentrations of:	>20 ppm <10 ppm	Barshad (1948)
Molybdenum toxicity in ruminants appears to involve not only an excess of molybdenum, but also low levels of copper and high sulfur-sulfate concentrations in forage. Copper supplementation of the diet appears to be only moderately effective in reducing toxicity dangers in cattle, but subcutaneous injections of copper-glycinate appears to afford protection for periods of 3 - 6 months.		Dye & O'Harra (1959)
Sulfate appears to increase excretion of molybdenum in animals.		Dick (1956)
It is possible for copper reserves of livestock to increase on low copper intakes when molybdenum and sulfate content of the diet are low and conversely for animals copper reserves to be depleted even to a level of clinical copper deficiency when copper intake is normal and molybdenum and sulfate intake are high.		
The concentration in forage vegetation which appears to cause toxicity problems of molybdenum in grazing animals is reported as a range of:	10 - 20 ppm	Kubota et al. (1967)
Molybdenum appears to exhibit a toxicity at concentration levels very similar to that of arsenic. In monogastric animals, only slight toxicity appeared at intake levels of:	50 ppm	Frank & Moxon (1937)
From the literature reviewed, the upper limit of molybdenum concentration in vegetation for good animal nutrition appears to be in a range of: The desirable range of molybdenum content of forage between nutritional deficiency in the crop and toxicity in livestock is quite narrow.	5 - 10 ppm	James et al. (1968)

	Concentration	Reference
Severe symptoms of molybdenum toxicity were observed in cattle grazing on native pastures which contained concentrations of molybdenum from normal to 160 ppm.		Becker et al. (1965)
Molybdenum appears to be essential in the animal diet in that it has been found as a constituent of the enzyme xanthine oxidase, which appears to play an essential role in purine metabolism in animals.		Maynard & Loosli (1969)
Molybdenum toxicity appears to occur in livestock on pastures with vegetation containing levels of more than:		Muir (1941)
A potential hazard may exist where pastures contain:	14 ppm	
	7 - 14 ppm	
Toxicity was observed in cattle at intake levels of:	10.3 ppm	Britton & Goss (1942)
The concentration range for vegetation where the toxicity occurred:	6 - 36 ppm	
Molybdenosis has been reported in Nevada on daily dietary intakes as follows:		Dye (1962)
cattle:	5 - 6 ppm	
sheep:	10 - 12 ppm	
Nickel:		
There have been no reports of widespread damage to the environment by nickel compounds in the atmosphere or elsewhere, and nickel does not appear to be a problem with respect to its effects on vegetation, domestic animals or wildlife.		Smith (1972)
Studies indicate that 90% of the ingested nickel in dogs is excreted in the stool and 10% eliminated in the urine. A complete balance study in a dog before and after exposure to nickel carbonyl indicates that virtually all of the nickel is excreted within six days and there is no significant retention of nickel in the body.		Tedeschi & Sunderman (1957)
Selenium:		
Growth retardation and death has occurred in rats and guinea pigs after several weeks on a diet of wheat containing:	8 - 10 ppm	Nelson et al. (1933)
Symptoms of intoxication from selenium were observed when blood levels began to exceed:	3.0 ppm	Maag et al. (1960)
Loss of appetite and depression in cattle began to appear at selenium blood levels of approximately:	4.0 ppm	
Alkali disease appears to be the predominant animal disease in areas where seleniferous soils are formed. The disease results from the consumption of grains and forages for a period of several days or weeks that contain up to:	25 ppm	Moxon & Rhian (1943)
Symptoms include dullness and lack of vitality with animals becoming emaciated, stiff, and lame. The prominent symptoms in horses and mules appears to be the loss of long hair from the mane and tail.		

	Concentration	Reference
Symptoms of selenium toxicity in cattle: early stages show a dullness and lack of vitality. There appears to be a stasis of the gastrointestinal tract. There also appears to be considerable abdominal pain with grunting, grating of teeth and salivation. Animals have been observed to wander, often aimlessly in circles. There may be impairment of vision. Prior to death, paralysis may result.		Beath et al. (1934)
In poultry, it was found that the feed consumption and growth of chicks is reduced when a ration is fed which contains:		Moxon (1937)
Infertile eggs and deformed embryos have resulted when hens received a ration containing selenium at levels of:	8.0 ppm	
	3.5 ppm	
From a review of the literature, it appears that chronic toxicity in various animals will occur at the following selenium levels in feeds:		Thacker (1961)
Chickens:	5 - 8 ppm	
Cows:	5 - 40 ppm	
Dogs:	7.2 - 10 ppm	
Rats:	5 - 15 ppm	
Sheep:	10 mgs/day	
Swine:	10 - 15 ppm	
Tests show the administration of subtoxic levels of selenium produce an increase in clean fleece weight, fiber thickness, and body weight in sheep. Data suggests selenium may be an essential nutrient for wool and body growth in sheep.		Slen et al. (1961)
In chronic cases of alkali disease, there appears to be a loss of hair from the mane and tails in horses, tails in cattle, and a general loss of hair in swine. Hoofs slough off, lameness occurs, food consumption decreases and death may occur by starvation. Soil considered to be potentially hazardous to livestock is any soil which contains in excess of:		Maynard & Loosli (1969)
Chronic toxicity is caused by rations as little as:	0.5 ppm	
Young animals are especially susceptible and growth is retarded with levels too low to cause other evident symptoms.	8.5 ppm	
Selenium is essential in the diet of livestock to prevent the deficiency syndrome of white muscle disease. The critical required level of selenium in the animal in order to prevent white muscle disease has been stated as:	0.1 ppm	Allaway & Hodgson (1964)
In laboratory experiments with rats receiving a subtoxic dose of sodium selenite, it has been noted that the injection of arsenite showed a marked increase in the excretion of selenium into the gastrointestinal tract.		Ganther & Baumann (1962)
From a study in South Dakota, it has been observed that cattle have shown symptoms of chronic selenium toxicity on grass diets containing selenium at levels of:	10 - 20 ppm	Moxon (1958)

Vanadium:	Concentration	Reference
Vanadium occurs in all animals and is accumulated in large amount by ascidians and holothuroidians. Vanadium is probably essential to vertebrates and has been shown to decrease dental caries in animals and children. Vanadium appears to inhibit the biosynthesis of cholesterol in both animals and man.		Cannon (1963)
In studies with laboratory animals receiving suboptimal diets, vanadium pentoxide caused toxicity at concentrations of:	100 ppm	Stokinger (1963)
In animals receiving optimal diets, toxicity appeared at concentrations of:	1000 ppm	
Zinc:		
No ill effects were observed in lactating cows when fed a diet over a six week period with a daily zinc concentration of:	1269 ppm	Miller et al. (1965)
Weight gain and feed consumption were reduced in cattle receiving a diet containing:	900 ppm	Ott et al. (1966)
No adverse effects were observed in cattle receiving a dietary zinc concentration of:	500 ppm	
When cadmium was given in concentrations of 350 ppm, there appeared to be reduced zinc absorption in calves. Cadmium appears to be a strong anti-metabolite for zinc. Whether the effect in zinc absorption is direct or indirect is unknown.		Powell et al. (1967)
Zinc is an essential element in animal nutrition. Studies indicate the primary agricultural problem with zinc is that of livestock and plant deficiencies. Prevention of zinc deficiency in cattle requires a dietary level of approximately:	8 ppm	Maynard & Loosli (1969)
Zinc intoxication in pigs has been observed at dietary concentrations of:	2000 ppm	
Death has resulted in lambs receiving a dose of zinc at concentrations of:	4 - 6 grams	Ott et al. (1966)
Zinc concentrations in plants have a low availability to animals. This has been attributed to the presence of insoluble complexes of zinc with calcium and phytic acid in plants.		Allaway (1968)
On studies concerning zinc, it was noted that in one example, zinc deficiency was induced in calves receiving a purified diet with a zinc content of:	<10 ppm	Kubota & Allaway (1972)
It has been estimated that fattening rations used for optimum rates of gain for steers should contain zinc levels of:	40 ppm	

Fluoride:	Concentration	Reference
Symptoms of fluorosis appear to be difficulty in locomotion, raggedness of coat, reduction of milk yield, and abnormal skeletal development. Morphological changes are manifested in the bones and teeth. Bones become soft and teeth become pitted and eroded. Toxicity depends on: nature of the fluoride compound, duration and mode of intake, along with the species and age of the animal.		Pierce (1939)
Chronic fluorine toxicosis is the type most commonly observed in livestock. The onset appears as a chronic debilitating disease. Because of the nature of the symptoms, it appears to be impossible to define a precise point at which excessive continual consumption of fluorides induce chronic fluorosis. Fluoride toxicity can be observed by the development of fluorotic dental lesions in animals during tooth development. Fluorides are stored in the bones and over a period of time will cause structural changes. Bone lesions are characteristic of chronic fluorosis. Chronic fluorosis has been observed in dairy cattle after 2 1/2 years of daily dietary intake of: 93 ppm Chronic fluorosis has also been observed in dairy cattle after 4 1/2 years on a daily intake of: 49 ppm		Shupe (1969)
From data on cattle, the soft tissues do not appear to retain increased dietary fluorides with the exception of the kidney. The bones appear to store fluorides until they become saturated. At the bone saturation point, the excess fluorides begin to spill over into the soft tissues and the early symptoms of fluoride toxicosis begin to appear. This time period for bone saturation to take place has been called the lag period.		Phillips & Suttie (1960)
The margin of concentration ranges of dietary intake of fluorides between physiologic benefit and toxicity is very small. Toxicity resulting from fluorides is usually from three principal sources: water, feed supplements, and ingestion or inhalation of fumes and dust from industrial sources. The safe and harmful levels of dietary fluorine depend upon type compound, time duration of ingestion, animal species, and the age of the animals.		Underwood (1962)
Grazing animals receive fluoride principally from fluoride dust on foliage. The borderline forage concentration for possible fluorosis in dairy cattle appears to be in the range of:	30 - 40 ppm	Hodge & Smith (1972)

	Concentration	Reference
Animals may be subject to fluoride toxicity when grazing on vegetation with a level of approximately:	50 ppm	Phillips et al. (1955)
Fluoride injury to animals depends upon their total fluoride intake rather than the fluoride concentration in any particular portion of the diet. Contamination of forage by wind blown soil dust or soil splash during heavy rain and consumption of soil under close grazing conditions may contribute appreciably to fluoride injury to animals in areas where high soil fluoride exists.		Pack & Adams (1966)
A concentration of fluorine in the total ration of animals which has been termed as borderline between safe and unsafe dietary intakes is given at a level of (on a dry weight basis)	100 ppm	Mitchell (1942)
The normal dietary ingestion of fluoride in cattle of dry forage matter is listed at:	15 ppm	Shupe et al. (1964)
Concentrations of fluorides in feed stuffs which have shown toxic effects are as follows:		
borderline symptoms:	30 - 40 ppm	
moderate symptoms:	40 - 60 ppm	
severe symptoms:	60 - 109 ppm	
Toxicity at these concentrations require ingestion over long periods of time.		
Fluorine tolerances in various livestock diets of breeding and lactating animals:		Shupe (1969)
dairy and beef heifers:	30 ppm	
dairy cows:	30 ppm	
beef cows:	40 ppm	
sheep:	50 ppm	
swine:	70 ppm	
Fluorine tolerance in finishing animals with average feeding periods:		
beef and dairy heifers:	100 ppm	
dairy cows: approximately	100 ppm	
beef cows: approximately	100 ppm	
sheep:	160 ppm	
Cattle will withstand an ingestion of soluble fluoride in total feed up to levels of approximately:	75 ppm	Elmslie (1936)
Sulfur:		
Pathological changes have been observed in the lungs of laboratory animals after two weeks exposure to sulfuric acid mists at a level of:	1 mg/m ³	Bushtueva (1962)
Green plants are the primary source of sulfur for animals which are unable to form proteins from inorganic sulfates. Inorganic sulfur cannot be utilized by animals and sulfur in the elemental form is toxic.		Gilbert (1951)
Sulfuric acid aerosols are more important factors in causing ill effects to animals than is sulfur dioxide.		Middlton (1966)

The Effects of Selected Trace Elements
on Human Health

Arsenic:	Concentration	Reference
Most toxic of the arsenic compounds is arsenic gas and can cause death at:	100 ppm	Lee (1972)
<p>Toxicity symptoms in humans: weakness, abdominal pain, generally non-specific complaints. Symptoms associated with occupational exposure: dermatitis, perforation of nasal septum, and occasional ulceration of skin.</p> <p>Chronic effects of arsenic on humans: dermatitis, hyperpigmentation, conjunctivitis, nasal irritation, edema of eyelids, hoarseness, loss of hair, CNS disorders, nausea, vomiting, abdominal pain, hypoplastic anemia. Acute toxicity effects: headache, dizziness, garlic odor of breath, chills, tingling of hands and feet, nausea, vomiting, abdominal cramping, pulmonary edema, hepatomegaly, hematuria, oliguria, albuminuria, leukocytosis.</p>		International Technical Information Institute (1976)
Beryllium:		Tepper (1972)
<p>When beryllium or its compounds are present as airborne particulates of respirable size, a hazardous situation may exist since inhalation of beryllium materials has been associated with both acute and chronic illness in humans. Potential problems of beryllium are related to concentration and size of particles in industrial and ambient atmospheres. All reported cases of beryllium disease have arisen from industry. The industries are: beryllium extraction, fluorescent lamp production, neon lamp industry, x-ray tube production, nuclear energy industries, alloy production, metal working, and electron tube production.</p> <p>Acute beryllium disease in humans usually lasts less than a year. The most important aspect of the disease is acute beryllium pneumonitis. This condition may be fatal. Acute disease arises largely out of short-term, accidental over-exposure. Chronic beryllium disease is marked by progressive pulmonary disease and cardiac complications. The prognosis in chronic disease is usually unfavorable.</p> <p>The threshold limit value for human exposure to beryllium compounds on an 8-hour time-weighted average is:</p>	0.002 mg/m ³ (air)	American Conference of Governmental Industrial Hygienists (1975)
Cadmium:		Fleischer et al. (1974)
<p>Estimated average daily intake of Cd in humans:</p> <p>Intestinal absorption is low, approximately 3 - 8%. Cadmium is concentrated in the liver and kidneys which contain approximately 50 - 75% of the body burden.</p>	20 - 50 mg/day	

	Concentration	Reference
Study indicates cadmium is not retained in any significant quantity in human body tissue with the major portion being excreted. Absorption of cadmium through the intestinal tract appears to be relatively limited. Renal damage in humans is likely to occur at cadmium concentrations in the outer cortex of the kidney of:	200 ppm	Friberg et al. (1971)
Chronic Cd emphysema may appear after long periods of exposure to levels of:	3 - 15 mg/m ³ (air)	
In fatal cases of acute Cd poisoning, significant pathological changes have been seen in the kidneys. Transient proteinuria has been detected in individuals with non-lethal cadmium exposure. Cadmium is not known to be concentrated in bone tissue. Anemia has been observed in workers exposed to cadmium oxide dust. The evidence that cadmium may act as a carcinogen in man is not yet conclusive.		
Pulmonary emphysema is one of the primary symptoms of chronic cadmium poisoning due to long-term inhalation of Cd fumes, cadmium oxide dust, or cadmium salt. Kidney damage is also considered to be a classic syndrome of chronic poisoning.		Bonnell (1965)
Estimated dose of cadmium causing appearance of toxicity symptoms in humans: Symptoms: Acute nausea and vomiting which may be followed by severe gastroenteritis.	15 - 30 mgms	Gleason (1969)
There may be an increased incidence of renal stones occurring in individuals who have had long-term exposure to cadmium dust.		Ahlmark (1961)
In humans, toxic levels of cadmium by inhalation vary from:	1 - 30 mg/m ³ (air)	Browning (1961)
A positive association may be found between cadmium content of air and mortality ratios associated with heart disease.		Carroll (1966)
Study implicated high levels of cadmium in the kidney as a possible factor of hypertensive disease in humans.		Schroeder (1965)
Cadmium in foods may be capable of producing toxicity symptoms in man at concentrations of:	15 ppm	Underwood (1962)
Acute cadmium response syndrome is characterized by severe nausea, salivation, vomiting, diarrhea, abdominal pains, and myalgia. Liver and/or kidney damage may follow or accompany the development of acute signs. Involvement of the respiratory system may also accompany acute signs. Serious symptoms have appeared with intake of:	10 mgms	Arena (1963)

	Concentration	Reference
Chronic effects of inhaled cadmium include total or partial loss of smell, cough, labored breathing, weight loss, and yellow staining of the teeth.		
Chromium:		
Chromium appears to accumulate in the lungs with increasing human age. It is quite insoluble and appears not to interchange with the rest of chromium body stores. The insoluble compounds appear to be primarily chromium chlorides.		Baetjer (1959)
Trivalent chromium complexes appear to be an essential factor in the control of glucose metabolism. Abnormal glucose tolerances have occurred where a deficiency in trivalent chromium exists.		Schwartz & Mertz (1959)
Trivalent chromium supplementation may improve to glucose tolerance of adults with the response of tolerance improvement indicating a possible marginal deficiency.		Doisey et al. (1968)
In the industrial environment, chronic chromium over-exposure appears usually as a general inflammation of the respiratory system with possible perforation or ulceration of the nasal septum.		Smith (1972)
Copper:		
Daily adult copper requirement: not considered a health hazard except in very large doses.	1 mg	Soukup (1972)
Lethal dose of copper for humans: Symptoms of copper toxicity from single high exposure are usually gastric in nature.	18,000 mg/kg body wt.	International Technical Information Institute (1976)
Maximum T.L.V. of copper fumes in the work environment: (8-hour time-weighted average)	1 mg/m ³	American Conference of Governmental Industrial Hygienists (1975)
Wilson's disease is the only significant copper toxicity in man. It is an inherited autosomal recessive trait where even normal copper intake accumulates in the vital organs to toxic concentrations.		Scheinberg (1969)
Lead:		
The largest tolerated amount of lead in drinking water for humans appears to be reported in a range of:	0.35 - 2.0 ppm	Cantarow & Trumper (1944)
Under average conditions, lead is taken in at approximately daily rates of 300 micrograms from air. About 10% of inhaled lead is absorbed and 10 - 50% of inhaled lead. The human threshold for lead intake on a daily basis is approximately:	600 µg/day	Lagerwerff (1972)
Long duration intake of soluble lead compounds by humans may cause adverse symptoms at a level of:	1000 µg/day	Kehoe (1966)

Concentration	Reference
Under urban conditions, it appears that an appreciable portion of the total human body burden of lead is contributed by inhalation. It is not yet possible to evaluate the significance of small increases in the total body burden of lead from atmospheric sources, but the evidence from industrial workers has not shown any harmful effect.	Kanzantia (1973)
Mercury:	
The most common form of mercury found in the environment and that which is most toxic to man is methyl mercury. Studies indicate that intestinal absorption is between 90 and 95%.	Grant (1971)
It has been shown that methyl mercury has the ability to penetrate the placental barrier and produce fetal damage at levels which have not produced symptoms in the mother.	
The concentration of mercury expected in the diet from natural background levels and environmental contamination is:	0.02 - 0.05 ppm
The various hazardous concentrations previously reported in the literature for mercury compounds are as follows:	Grant (1971)
possible chromosome damage:	0.02 ppm
possible fetal damage:	0.40 ppm
symptoms of toxicity:	0.4 - 1.0 ppm
Mercury access to the body is gained mainly through the respiratory tract but absorption also takes place through the skin or by ingestion. Mercury inhibits some enzymes, produces potassium ion loss, blocks glucose uptake by erythrocytes and muscle, causes lesions of the central nervous system and influences bioelectric phenomenon by altering transmembrane potentials and by blocking nerve conduction.	Neville (1967)
Mercury may enter the body by inhalation, ingestion, or through the skin. Symptoms of toxicity fall into two classes. These are one with stomatitis, colitis, and nephritis predominating, and the other with tremor, and neurological symptoms.	Neal (1938)
One-half gram of mercuric chloride can be a lethal dose in humans causing shock, ulceration of the gastrointestinal tract, and destruction of the tubular epithelium of the kidney.	Kanzantia (1965)
Most frequent route of administration of methyl mercury is ingestion of protein-bound methyl mercury in food items. The earliest symptoms include fatigue, headache, and reduction in the powers of concentration and memory. A period of up to seven months may be required for appearance of nervous disorders.	Whitehead (1965)

Concentration	Reference
A concentration of 0.2 ppm in whole blood of methyl mercury is considered the minimum level for neurotoxic exposures in humans. There is some uncertainty as to what constitutes lethal concentrations of methyl mercury in man.	Hammond (1971)
At air concentrations of 60 $\mu\text{g}/\text{m}^3$ of mercury vapor, the total amount appears to be retained in the lungs. Studies indicate almost total absorption of mercury vapor into the lungs.	Shepherd (1941)
Acute mercury intoxication has resulted in humans from inhalation of mercury vapor at arial concentrations of:	Stokinger (1963)
1200-8500 $\mu\text{g}/\text{m}^3$	
In the industrial environment, workers have been exposed to inorganic mercury compounds for a period of more than two years with no evidence of mercury intoxication at air concentratons of:	Kleinfeld (1961)
80 - 400 $\mu\text{g}/\text{m}^3$	
Molybdenum:	
There appears to be an interest in the role of molybdenum in human nutrition since studies in New Zealand and England show that children born and reared in high soil molybdenum areas have better teeth than do children in other areas of the countries.	Kubota & Allaway (1972)
Nickel:	
Nickel appears to be poorly absorbed from the ordinary human diet. The fecal excretion of nickel appears to be quite high as opposed to urinary excretion which indicates nickel is poorly absorbed in the gastrointestinal tract.	Horak & Sunderman (1973)
The concern of the effect of atmospheric nickel levels on the health of humans is based on evidence that certain nickel compounds are known to be carcinogenic to man and animals. The nickel levels required to produce observable effects in humans are considerably greater than those found in ambient air. The primary damage of nickel to humans is found in the industrial environment. The most toxic of all nickel compounds used in industry is nickel carbonyl. The threshold limit value of exposure in humans for nickel carbonyl is 0.0001 ppm, making it the most toxic gas on the entire list of substances for which TLV's have been established.	Smith (1972)
Selenium:	
It has been stated that the maximum amount of selenium in the total diet that a human can consume without selenium intoxication appears to be approximately:	Taylor (1952)

3 ppm

Concentration	Reference
In a literature review concerning selenium in human nutrition, no definite conclusions have been reached. Symptoms comparable to those of selenized domestic animals are essentially lacking. Cases of arthritis have been associated with selenium in the diet. There is some suspicion that other features such as discoloration of skin, bad teeth, dermatitis, and gastrointestinal disorders may be aggravated by the intake of small amounts of selenium.	Thacker (1961)
From a study by Lemley, human cases of selenium poisoning are more likely to occur from the use of selenium in industry than from the consumption of foods in the areas of seleniferous soils in the U.S.	Moxon (1958)
Selenium concentration considered dangerous to humans are: Food levels: 5.0 ppm Milk or water levels: 0.5 ppm	
In seleniferous areas of North America, disease conditions in man definitely attributable to selenium poisoning have yet to be demonstrated. There is no direct evidence of humans being affected by high seleniferous soils.	Underwood (1962)
Vanadium:	
Persistent cough has been observed in humans for periods up to eight weeks after exposure to vanadium pentoxide at air concentrations of: 1000 $\mu\text{g}/\text{m}^3$	Zenz (1967)
A number of workers were exposed to vanadium pentoxide at concentrations ranging from 18-925 $\mu\text{g}/\text{m}^3$ of air. Results showed that serum cholesterol levels were reduced approximately 10% below that of normal levels.	Lewis (1959)
In a study in England, it was found that the mortality from lung cancer appears to correlate significantly with the concentration of vanadium and particulates in the air. The concentrations of vanadium showed a strong association with the incidence of bronchitis in males. Vanadium and beryllium were found to be associated with the incidence of pneumonia.	Stocks (1960)
The lethal dose of vanadium through inhalation by man appears to be in a range of: 60,000-120,000 $\mu\text{g}/\text{m}^3$	Stokinger (1963)
Symptoms of vanadium poisoning observed in occupationally exposed groups include: paroxysmal cough, irritation of the throat, eyes, and nose, anorexia, tremors, hysteria, melancholia, and anemia accompanied by reduction in hemoglobin and the number of erythrocytes.	Athanasiadis (1969)

Zinc:	Concentration	Reference
In a reported study, increasing concentrations of soil-applied zinc did not significantly increase the element level in plant seeds. Since seed and fruits are major sources of plant material in human diets, it may be that very substantial increases in the level of available zinc in soils would have only slight effects upon the level of zinc in human diets.		Allaway (1968)
Zinc chloride has a TLV of: Toxicity symptoms: conjunctivitis parotis, popular dermatitis and ulceration of the fingers and hands.	1 mg/m ³ air	International Technical Information Institute (1976)
Toxicity of zinc chloride from inhalation shows the following symptoms: irritation of the nose and throat, headache, hoarseness, cough, chest pain, fever, nausea and vomiting, shortness of breath, and asthma along with pulmonary edema.		
Zinc oxide has a TLV of: This substance is the chief cause of metal fume fever.	5 mg/m ³ air	
Symptoms: hacking cough, moderate substernal pain, headache, nausea, vomiting, metallic taste, chilling and fever, pain in muscles and joints, marked thirst, and occasionally pneumonia.		
The ingestion of toxic amounts of zinc in food by humans produces an acute transitory illness within a few minutes after ingestion. Symptoms include: dizziness, tightness of throat, emesis, colic, and diarrhea.		Vallee (1959)
The problem of metal fume fever occupies the most prominent role among the possible toxic effects of zinc for humans.		
Fluoride:		
In man, a steady intake of 0.1 to 0.15 mg/kg body weight per day in drinking water has occasionally shown mottling of the enamel of the teeth.		Pierce (1939)
The oral lethal dose of fluorides in their soluble form for humans is given in a range of: Daily fluoride intake in community water supplies which has produced a disfiguring malformation of the enamel surfaces of teeth is given at:	5 - 10 grams 2 - 8 ppm	Smith & Hodge (1965)
Man inhaling ambient air containing less than 0.05 g/m ³ and retaining all of it would absorb negligible amounts of fluorides.		Hodge & Smith (1972)
In children, the mottling of teeth has occurred on regular drinking water intakes of fluoride at concentrations of:	2 - 5 ppm	Maynard & Loosli (1969)

	Concentration	Reference
Fluoride concentrations in the domestic water supply which has been established as beneficial in preventing dental caries or tooth decay in humans is:	1 ppm	Mitchell & Edman (1945)
Fluoride intake in the drinking water of humans over a period of approximately ten years has caused no significant histological changes in the bone structure at concentrations of:	0.1 - 4.0 ppm	Zipkin et al. (1958)
Fluorine does not appear to be a dietary essential. The only value to the body appears to be the limited promotion of resistance to dental caries.		Maurer & Day (1957)
Sulfur:		
Eighty percent of urban atmospheric sulfate has been found to be associated with particles below 2 μ m in diameter. The small sizes are easily respirable and can penetrate deeply into the lung surfaces.		Hagman et al. (1967)
Sulfur dioxide is a mild respiratory irritant, one of the basic effects is to produce reflex and/or direct broncho-constriction.		Hausknecht (1974)
Decreases in respiratory air flow rates and tidal volume and increases in airway resistance have been observed after 10-minute exposure to sulfates at levels of:	0.35 mg/m ³	Sim & Pattie (1957)
The respiratory irritant effect of sulfur dioxide is enhanced by water aerosols and particle sizes of less than 1 μ m.		Snell & Luchsinger (1969)
The average odor threshold of sulfur dioxide in humans at one second exposure time is reported to be:	0.50 ppm	Dubrovakaya (1957)
Respiration and pulse rates in humans have been observed to increase after 10-minute exposures to sulfur dioxide at a concentration of:	1.0 ppm	Amdur and Melvin (1953)
The threshold for inducing measurable broncho-constriction in healthy people from sulfur dioxide for exposure periods of 1 - 5 minutes has been established at a concentration of:	1.6 ppm	Tomono (1961)

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